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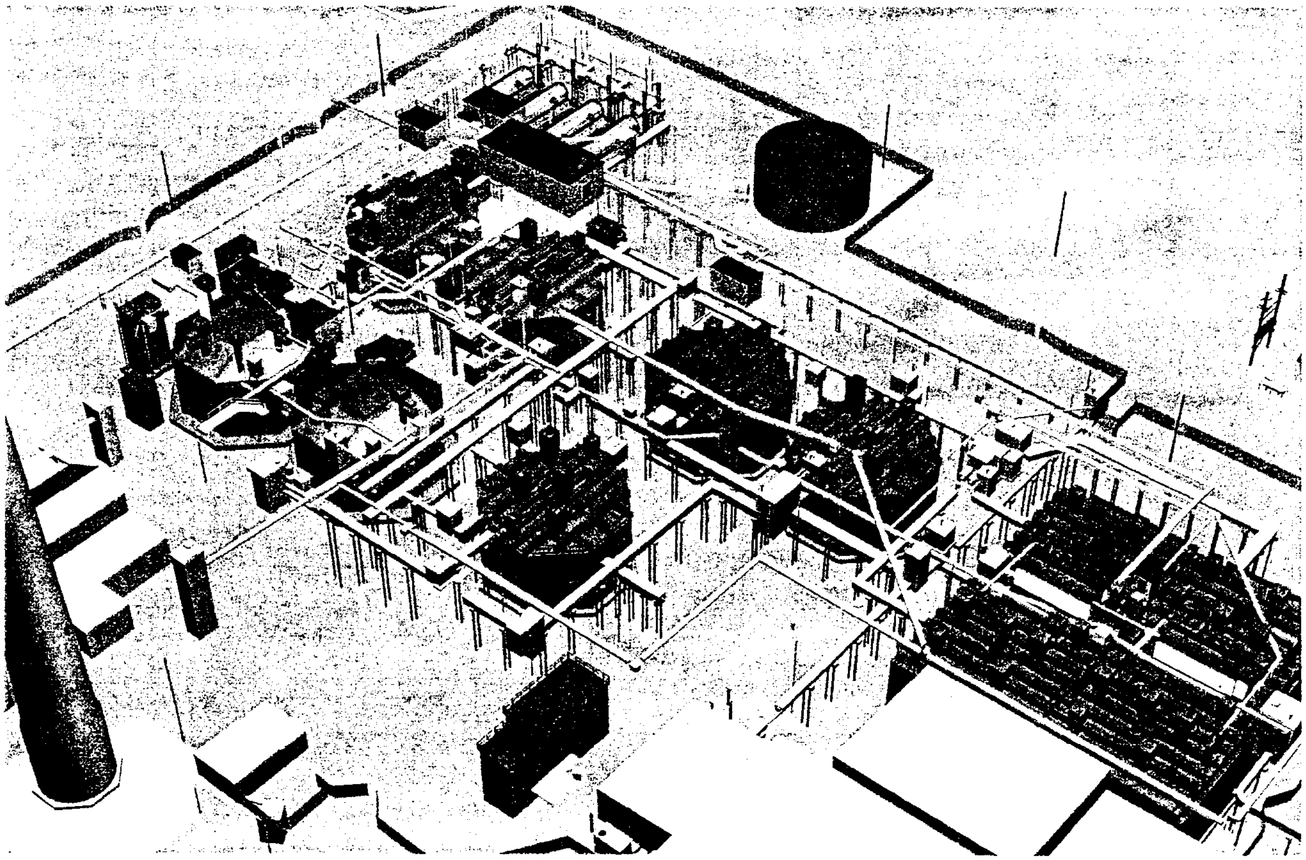
Project File: 015722

CONCEPTUAL DESIGN REPORT

BOOK 6: EDFs

Volume 2 of 3



INTEC TANK FARM FACILITY CLOSURE

INEEL
Idaho National Engineering & Environmental Laboratory
BECHTEL BWXT IDAHO, LLC

INTEC TANK FARM CLOSURE CONCEPTUAL DESIGN REPORT

BOOK 1 GENERAL (Two Volumes)

Book 1 consists of design requirements, design descriptions, general project information, and summaries of EDFs. Book one provides an overall summary of the project and the approach to Tank Farm Closure. Where an EDF covers a subject in more detail, the EDF is referenced. EDFs reside in BOOK 6.

BOOK 2 JUSTIFICATION DOCUMENT

Book 2 provides the details and justification for the closure process selected for the INTEC Tank Farm. It includes an alternatives assessment and cost benefit analysis.

BOOK 3 MODELING AND ANIMATIONS (Two Volumes)

Book 3 consists of the 3D Model of the Tank Farm and various views of the model. In addition the closure sequence for WM-182 & WM-183 has been animated utilizing the 3D Model; and has been transferred to VHS tape. 3D views of each of the major closure steps are provided.

BOOK 4 MOCK-UPS (Two Volumes)

Book 4 provides details on the past, present, and future proof of process activities. Mock-up test plans, subcontracts, current data, and drawings are included.

BOOK 5 DRAWINGS

Book 5 contains the underground drawings, design drawings for equipment and systems, and four fully annotated 3D views of each of the Tanks.

BOOK 6 EDFS (Three Volumes)

Book 6 contains all of the EDFs developed under the Conceptual Design (FY 99 & 00). The EDFs are summarized throughout BOOK 1. EDFs developed prior to the Conceptual Design are not included, but are available upon request.

BOOK 7 LINE LISTS

Book 7 contains a complete set of underground drawings for the Tank Farm and a complete line list for all pipelines within the Tank Farm. The Line List is subdivided into sections referenced to the specific Tank to which the line is associated. In addition, abandoned line drawings and associated lines lists are provided.

BOOK 8 PHOTOS

Book 8 is a small subset of Tank Farm Photos and Mock-up Photos. An extensive photo library has been developed within the HLW Program and is available.

ENGINEERING DESIGN FILES
Volume 2 of 3

EDF-015722-034	Comparison of Existing Tank Farm Load Limits with Loads Proposed During the Tank Farm Closure Project	B. G. Harris	1/25/00
EDF-015722-035	Absorbing Free Liquids	M. Wilcox	2/28/00
EDF-015722-36	(Not Used)		
EDF-15722-037	PA Modeling Assumptions (Included in PA, not in this CDR)	Kevin Poor	April 19, 2000
EDF-15722-038	Closure Sequence for WM-184, 185, 186	Jim Benson	July17, 2000
EDF-15722-039	Pipeline Decontamination Assessment	Mike Wilcox	July 17, 2000
EDF-15722-040	Tank Farm Sludge Density Measurements	Adam Poloski	July 6, 2000
EDF-15722-041	Surrogate Sludge for Tank Farm Closure Mock-Up	Adam Poloski Mike Wilcox	July 17, 2000
EDF-15722-042	Integrated Surface Sequence	T. Langenwalter	July 17, 2000
EDF-015722-043	Grout Qualification	Ray Schwaller	6/1/00
EDF-15722-044	Tank Grout Requirements for 10 CFR 61 Class C Limits	David Thorne	6/21/00
EDF-15722-045	TFF Closure Regulatory Analysis	Kevin Poor Lisa Matis	6/1/00

ENGINEERING DESIGN FILE

1. Project File No. 15722 2. Project/Task Tank Farm Closure

3. Subtask Process

4. Title: Surrogate Sludge for Tank Farm Closure Mockups

5. Summary: An effort to create a surrogate sludge material for tank farm closure mockups is discussed. Visual data from the Light Duty Utility Arm, and empirical data from tank farm samples are evaluated against a number of possible surrogate materials. This evaluation produced a **kaolin clay/ alum floc** as a recommended surrogate. **Hydrated gypsum** should be added to increase the settling rate. **Iron oxide should also be added (prior to flocculation)** as a pigment. The exact quantities of these materials need to be determined quantitatively in an analytical laboratory environment.

While the sludge initially exhibits good characteristics, sludge aging can produce some unwanted effects:

- After aging two to three weeks, the solids seemed to settle significantly faster and the yield stress properties seemed to degrade.
- After approximately three weeks the kaolin/alum sludge had some algae growth. Therefore, a fungicide may be added to prevent biological activity.

Therefore, if the mockups are performed immediately following sludge production (within one to two weeks) this degradation and biological activity should be minimized.

6. Distribution (complete package):

Distribution (summary package only):

7. Review (R) and Approval (A) Signatures: (Minimum reviews and approvals are listed. Additional reviews/approvals may be added as necessary.)

	R/A	Printed Name	Signature	Date
Author	R	Adam Poloski	Adam Poloski	10/23/00
Author	R	Michael Wilcox	Michael R. Wilcox	10/23/00
Technical Review	R	Edward Wagner	Edward Wagner	10/26/00
Requestor	A	Edward Anderson	E. Anderson	10/31/00

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1 Introduction

Selection of a simulated solid surrogate to mimic the physical characteristics of sludge located in tank WM-182 and Tank WM-183 within the INTEC Tank Farm Facility (TFF) has been performed. This evaluation was based on TFF solids technical data acquired to date. It was determined that kaolin clay (pigmented with iron-oxide) flocculated by the addition of aluminum sulfate (alum) provides the basis for an effective surrogate. Calcium sulfate dihyrdate (hydrated gypsum) provides adjustment of settling rate and may provide refinement of particle size distribution. Quantitative work needs to be performed in order to develop final recipe ratios and parameters of the surrogate ingredients.

Mixed waste sludge needs to be removed from TFF tanks as part of the closure process to the maximum extent practical. The tanks will be closed in a phased approach with sludge (solids) being transferred to other TFF tanks in order to begin closure of the tanks as they are emptied. In order to manage the TFF solids, it desired to mimic the sludge for use in TFF closure mock-up work. The mock-up is planned to test processes and equipment such as sludge displacement by grout of varying slump rates, tank solids washing, and remote camera operation.

Development of a surrogate sludge and its use in TFF tank closure mock-up execution is useful for a variety of reasons:

- Provides for a measurement of the amount of sludge displaced from additions of grout of varying slump rates.
- Provides for a measurement of how the sludge is encapsulated or entrained within the grout.
- Provides for a measurement of cured grout/surrogate composite compressive strength.
- Provides a vehicle to measure the effectiveness of wash-ball tank operations on removing solids adhered to tank walls and solids suspension for removal via the steam inductor.
- Provides an arithmetic basis for sludge mass remaining in the tanks after washball and grouting operations to base radiological and hazardous source term calculations in support of TFF conceptual design closure.

2 Significant Factors

2.1 Visual Data

While not based on strict empirical data, visual observations of the sludge material provide a general understanding of the behavior of the solids. We have a great amount of video footage from the LDUA during inspections and sampling. A few of the more interesting scenes pertaining to the surrogate solids effort from the WM-182,WM-183 video collection have been selected. These selections will be discussed and some conclusions will be drawn based on these photographs. The first set of images consists of the LDUA inspecting prior WM-182 sampling locations (see Figure 1). The photograph on the left shows one previous sample location. This sample location shows cracks on the surface of the sludge layer. The cracks seem to indicate that the solids have solid-like properties. The photograph on the right shows a different sample location. This image shows the surface cracking similar to the other sample location. Therefore, this property is not localized. The right image also shows a distinct cylindrical shape at the sampling location. Since the LDUA sample port is cylindrical and the sample depression did not crumble to an angle of repose, this image also shows that the sludge layer acts solid-like in nature.

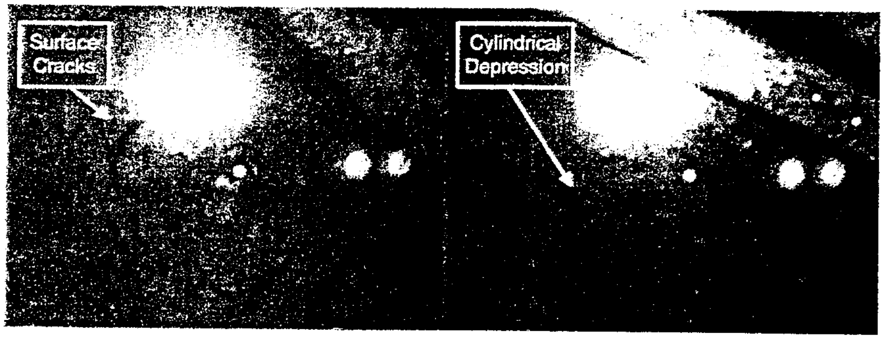

Figure 1: Inspection of Previous Sampling Locations (WM-182)

The second set of images consists of the LDUA inspecting a location where the sampler was previously moved through the WM-182 sludge layer (see Figure 2). The image on the right shows the original location where the sampler was placed in the sludge layer. Note the surface cracking is again present in this image. As the sampler was moved to the left, a wake developed behind the sampler. In this wake area, one can see relatively large solid clumps or agglomerates near the boundary of the wake area. Much smaller clumps are present in the center of the wake. This occurred because as the sampler was moved through the sludge layer large cracks would form near the wake boundary region. These cracks would eventually grow large enough to form large agglomerates. As these agglomerates move into the wake, larger shear rates are generated by the velocity gradient that break apart the agglomerates. Therefore, one could see the solid-like properties of the sludge under low shearing conditions at the wake boundary and fluid-like properties in the wake when the shear rates became large enough the break the agglomerates into smaller particles. Consequently, this material appears to act as a solid until a certain threshold is reached. At this point, the sludge begins to behave as a fluid. This is the definition of fluid dynamics property called a ***yield stress***. Sludges commonly possess this yield stress property.

Figure 3 shows a scene where the LDUA sampler was placed in the WM-182 sludge layer. As the sampler sat in the sludge layer, the LDUA mast was in the air above the tank. Gusts of wind oscillated the mast and in turn oscillated the sampler. As the sampler oscillated,

Figure 2: LDUA Sampler Moved Through The Sludge (WM-182)

an area of sludge around the sampler clearly oscillated with the sampler. While we could only observe the uppermost portion of the sludge layer, this situation demonstrates how the sludge layer possesses fluid-like properties.

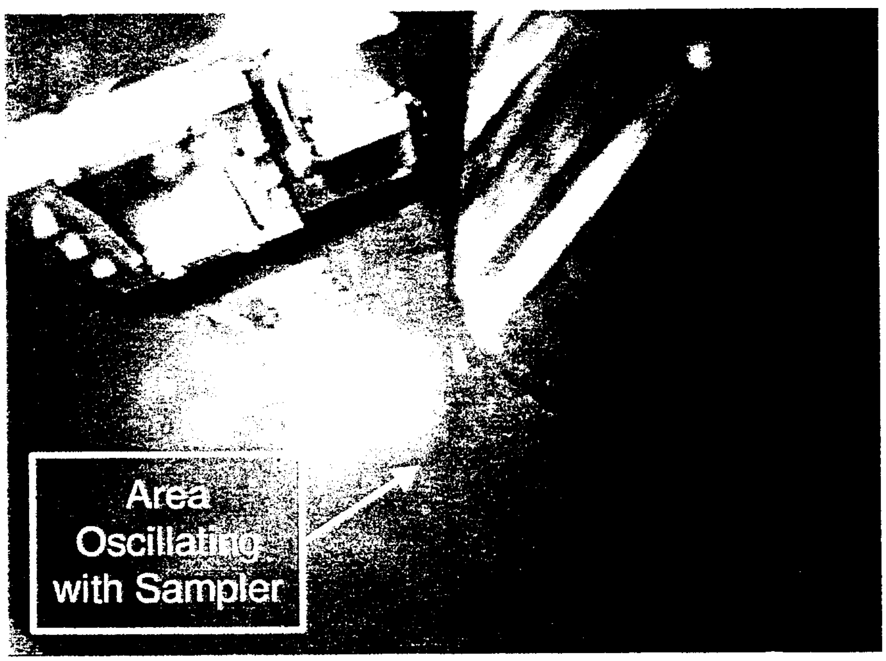

Figure 3: Sludge Layer Oscillating with Sampler (WM-182)

Figure 4 shows a scene where the LDUA sampler was taking a sample from the WM-182 sludge layer. As the sampling began, surface cracks (as previously discussed) could be seen forming. Near the end of the of the sampling a relatively large amount of agitated solids could be seen billowing out near the sampler. This situation can be interpreted as follows:

- The surface cracks are forming due to low shear stresses under the yield stress threshold.

As a result, the sludge particles act interdependently on each other and possess solid-like behavior.

- The billowy disturbance is generated due to larger shear forces that are above the yield stress threshold. As a result, the sludge particles act independently of each other and possess fluid-like behavior.

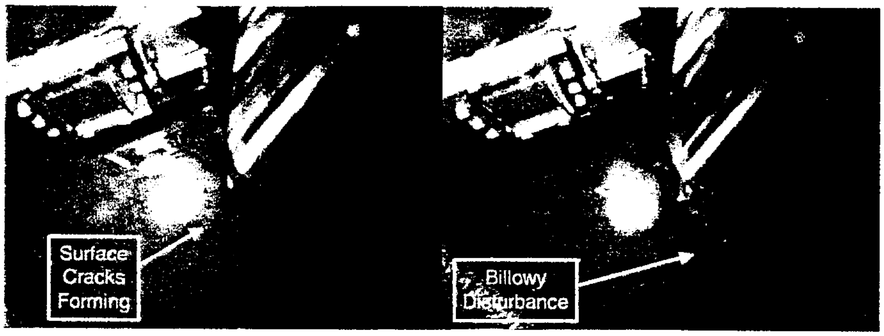

Figure 4: WM-182 Sludge Sampling

Figure 5 shows a scene where the LDUA sampler was taking a sample from the WM-183 sludge layer. The interesting feature in this scene is that while the WM-182 sludge layer was under a few inches of standing free liquid, the WM-183 sample location has no standing free liquid and the sludge layer is undersaturated. In this undersaturated condition the sludge layer appears to possess only fluid-like behavior. As the sampler is inserted, the sludge layer is pushed around the sampler in a fluid-like manner. When the sample is taken, no surface cracks form and the sludge could be likened to a thick mud.

Figure 5: WM-183 Sludge Sampling

Figure 6 shows the LDUA inspecting the WM-182 sludge. The images show particles floating on the surface of the standing liquid (see Figure 6). Under this layer of standing liquid one can see the settled sludge particles. This is interesting because previous sampling activities of tank liquid in the transfer lines have shown a relatively large amount of solids in the tank farm liquid. Many people have assumed these solids were due to suspended solids in the tank farm liquid. This image shows that the majority of the solids have settled out and some particles are suspended on the surface of the liquid due to surface tension. Consequently, the assumption that relatively large amounts of suspended undissolved solids ($3 \frac{g\ UDS}{L}$)in the tank farm liquid could be in error. The UDS concentration measurements are from liquid samples taken as the tank farm liquid was transferred from one tank to another via steam jet eductor. Figure 7 shows the sludge layer around a steam jet eductor in WM-183. As one can see, the steam jet not only transferred liquid but also entrained solids around the steam jet which may account for the large amount of "suspended" UDS.

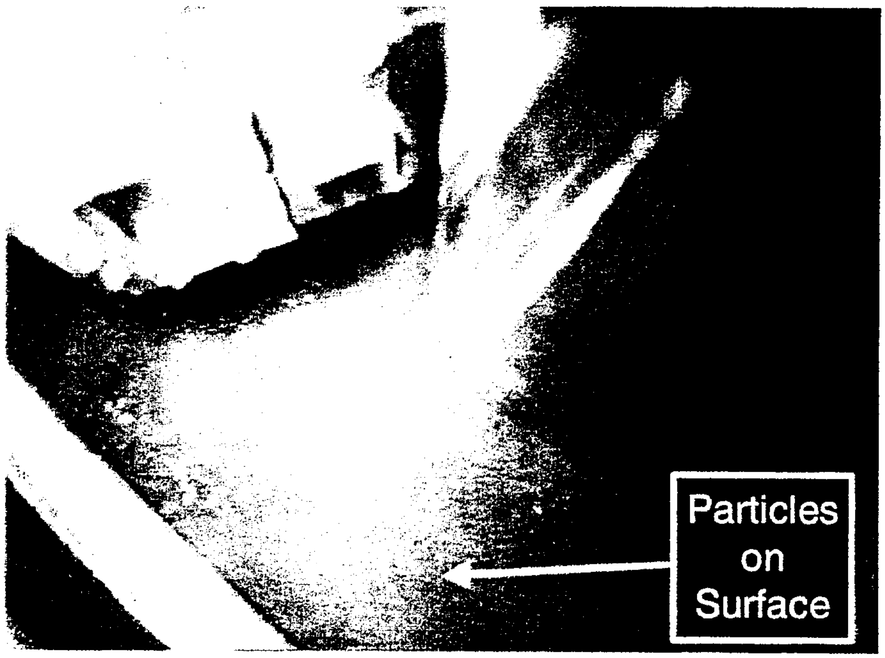

Figure 6: Particles Floating on Clear Liquid (WM-182)

One might argue that that once the depression around the steam jet is established the amount of entrained solids would be minimal. However, it seems that the required yield stress to agitate and move the solids is low and is met by simply transferring liquid from the tanks. Figure 8 shows the topology of the sludge layer in WM-183. After liquid was transferred from the tank, the topology of the sludge layer was significantly changed. This indicates that a significant amount of entrained solids could still be present after establishing a depression around the steam jet. If one used a different method to transfer the liquid, such as slowly removing the liquid from the top, the UDS concentration should be minimized.

Besides LDUA footage, a WM-182 sample was taken and placed in the RAL hot cell. Figure 9 shows this sample as it is tilted to one side. As one can see, the clear liquid top layer

Figure 7: WM-183 Steam Jet

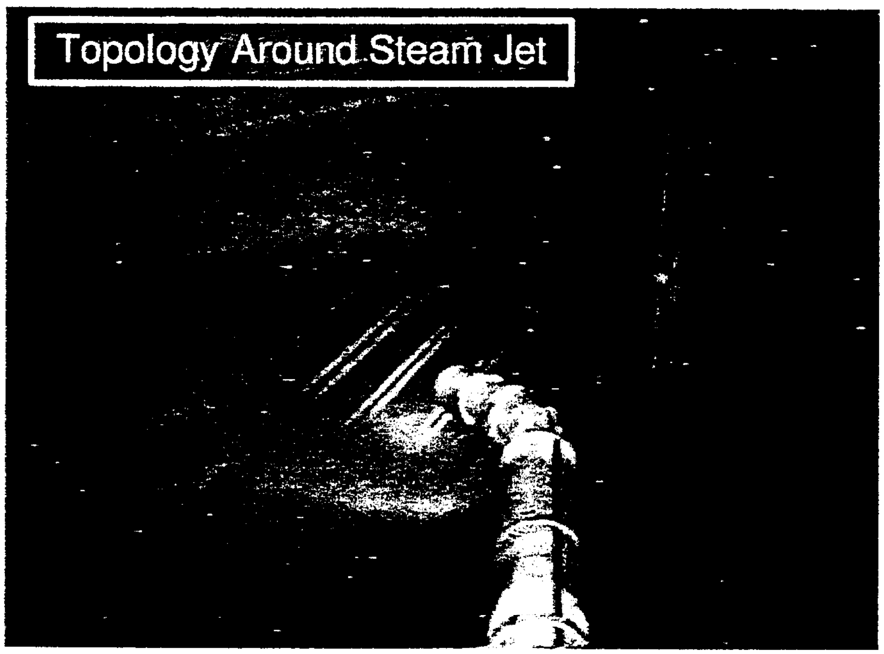

Figure 8: WM-183 Sludge Layer Topology

is fluid-like and moves with gravity. The sludge layer, however, is solid-like and remains in its settled configuration. This again is evidence of a yield stress property. As the bottle was tilted quickly from one side to another, the sludge particle would break apart and become agitated and billowy, thus clouding the clear liquid layer.

Figure 9: Tilting the WM-182 Hot Cell Sample

In conclusion, the visual data we have discussed above provides evidence for the following conclusions:

- The solids are electrostaticly attracted to each other. This attraction provides the observed yield stress phenomenon and solid-like behavior (surface cracks, tilted bottle, etc.).
- The electrostatic attraction is relatively weak and once these forces have been broken the particles act in a fluid-like manner. This explains the observed change in sludge layer topology, the wake behind the sampler, and the billowy disturbances.
- This electrostatic attraction is the driving force behind flocculation. Further evidence of the sludge being a floc will be presented below. See Appendix A for a brief discussion on flocculation.

2.2 Settling Type and Rate

For certain types of solid/liquid separation operations, an understanding of the dynamics involved in settling is essential. Perry's Chemical Engineers' Handbook [2] has a general discussion of various settling regimes:

> At low concentrations, the type of settling encountered is called particulate settling. Regardless of their nature, particles are sufficiently far apart to settle freely. Faster settling particles may collide with slower settling ones and, if they do not cohere, continue downward at their own specific rate. Those that do cohere will form floccules of a larger diameter that will settle at a rate greater than that of individual particles.
>
> There is a gradual transition from particulate settling into the zone-settling regime, where the particles are constrained to settle as a mass. The principal characteristic of this zone is that the settling rate of the mass, as observed in

batch tests, will be a function of the solids concentration (for any particular condition of flocculation, particle density, etc.).

The solids concentration ultimately will reach a level at which particle descent is restrained not only by the hydrodynamic forces but partially by mechanical support from the particles below; therefore, the weight of the particles in mutual contact can influence the rate of sedimentation of those at lower levels. This compression, as it is termed, will result in further solids concentration because of compaction of the individual floccules and partial filling of the interfloc voids by the deformed floccules. Accordingly, the rate of sedimentation in the compression regime is a function of both the solids concentration and the depth of pulp in this particular zone. As indicated in Figure 10, granular, nonflocculent particles may reach their ultimate solids concentration without passing through this regime.

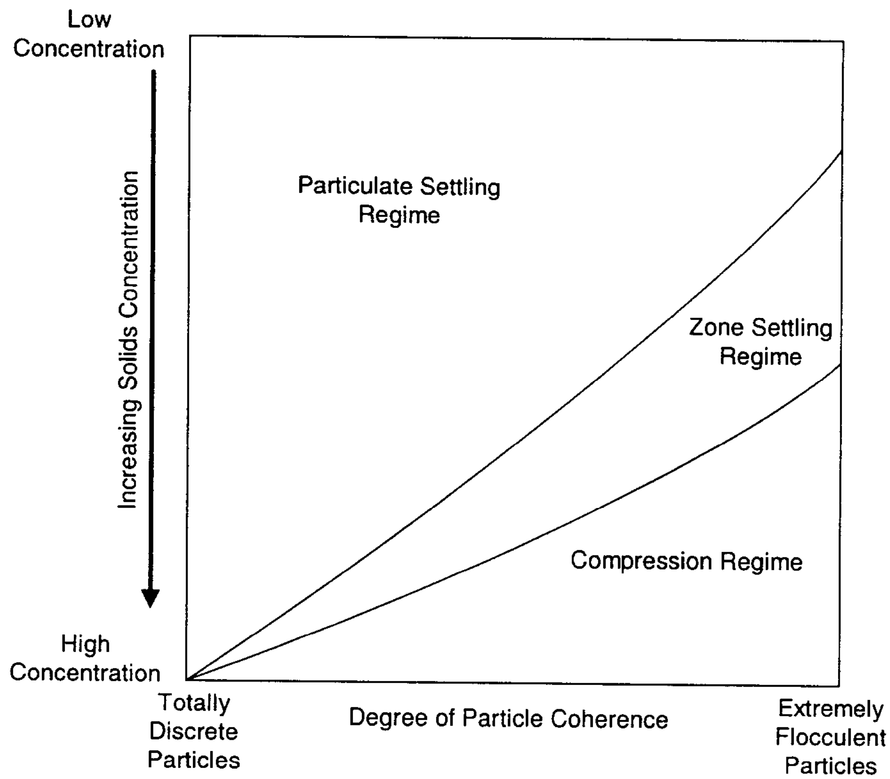

Figure 10: Settling Regimes

These types of settling are further discussed by Pierre and Ma [3]. In this paper, Pierre and Ma describe two types of settling, accumulation sedimentation, which is analogous to particulate settling, and flocculation sedimentation, which is analogous to zone/compression settling. These types of sedimentation are illustrated in Figure 11.

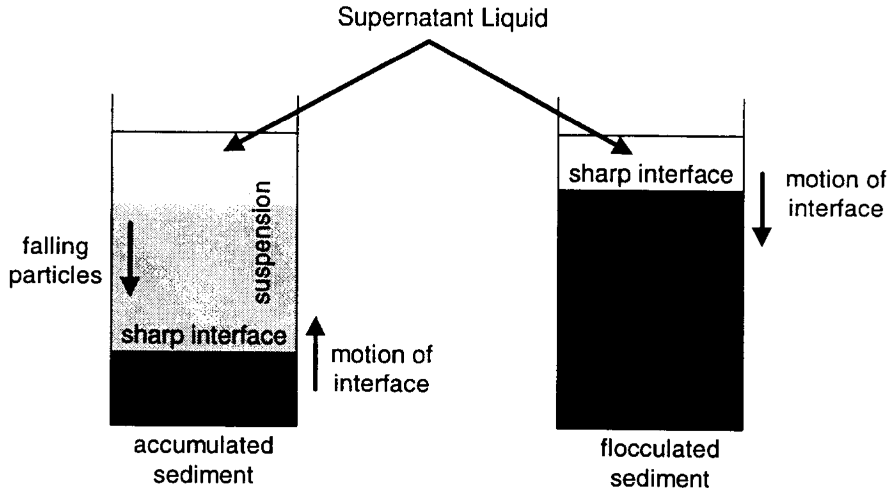

Figure 11: Accumulation Sedimentation and Flocculation Sedimentation

The WM-182 hot cell sludge sample was completely shaken and allowed to settle. Photographs were taken at various times after agitation. From the upper left photograph shown in Figure 12, one can see that we have a relatively high solids concentration. As a result, the degree of flocculation should be the determining factor in the type of settling that occurs. As time progresses after agitation, flocculation sedimentation or zone/compression settling is observed; indicating a relatively high degree of flocculation. From these pictures, we were able to scale the images to a similar sample bottle with a measured circumference and get the heights of the sample and settled sludge layer as a function of time. Nondimensionalizing the system involves using the following relation:

$$\text{Settled Solids Percent} = 100\% \times \frac{\mathrm{V_{sample}} - \mathrm{V_t}}{\mathrm{V_{sample}} - \mathrm{V_\infty}} \tag{1}$$

where,

V_{sample} is the total volume of the sample

V_t is the volume of the settled sludge layer at time t

V_∞ is the final settled volume of the sludge layer

From this equation, the plot shown in Figure 13 can be constructed. Note that there is no way to gauge the error involved in these data. Based on best professional judgment, a 20% error is assumed. A plot of the interface velocity as a function of time is shown in the same figure. From these photographs and plots, a slow flocculation sedimentation can be concluded.

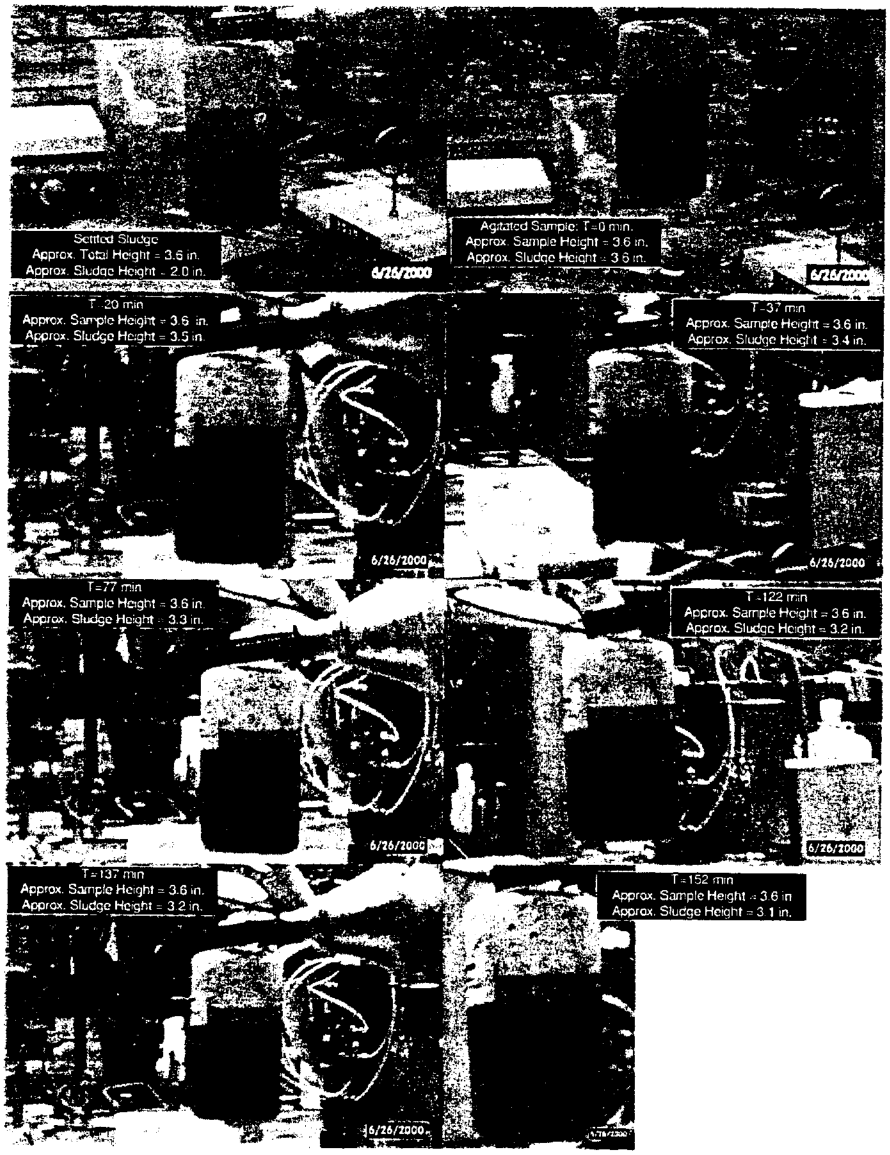

Figure 12: WM-182 Sludge Sample Settling Photographs

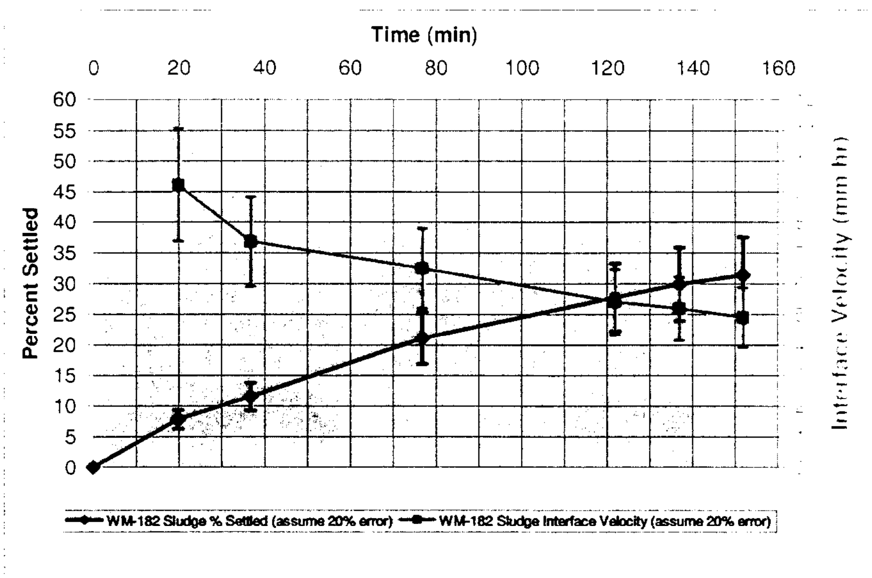

Figure 13: WM-182 Sludge Compression Settling Rate

2.3 Particle Size Distribution

A Horiba particle size analyzer was recently deployed in the RAL hot-cell. Several of the LDUA samples were analyzed using this particle size analyzer. The results of this analysis were compiled in "WM-182/183 Heel Slurry PSD Results Report" [5]. The particle size distribution (PSD) data in this report consists of two distributions for both WM-182 and WM-183. The first set of PSDs consists of data taken with the ultrasonic dispersion chamber turned off while the second set of data consists of PSDs with the ultrasonic dispersion chamber turned on. With the ultrasonic dispersion chamber off, the PSDs for both WM-182 and WM-183 were significantly shifted to the right (i.e. bigger particles, see Figure 14). This is expected since the ultrasonic dispersion chamber would disperse the floccules into their smaller "fundamental" component particles. For WM-182, the median sonicated particle size is approximately 8 μm. The WM-183 median sonicated particle size is approximately 12 μm. With the ultrasonic dispersion chamber off, the only thing to keep the particles from cohering to each other (i.e. flocculating) is the centrifugal recirculation pump (see Figure 15) which may or may not keep the system dispersed.

Perry's Chemical Engineers' Handbook [2] has a general discussion of interparticle attraction and particle size:

> Figure 10 illustrates the relationship between solids concentration, interparticle cohesiveness, and the type of sedimentation that may exist. "Totally discrete" particles include many mineral particles (usually greater than 20 μm), salt crystals, and similar substances that have little tendency to cohere. "Flocculent" particles generally will include those smaller than 20 μm (unless present in a

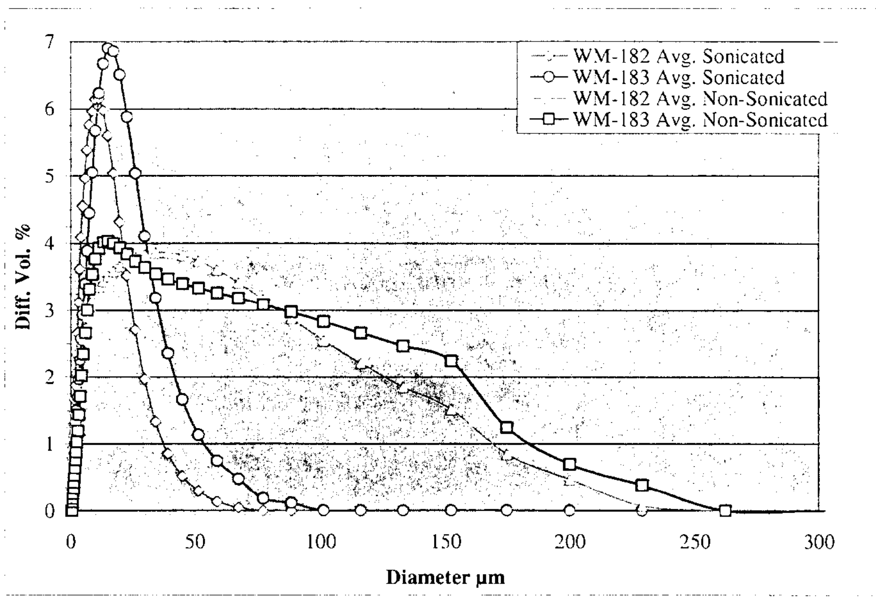

Figure 14: WM-182 and WM-183 Particle Size Distributions

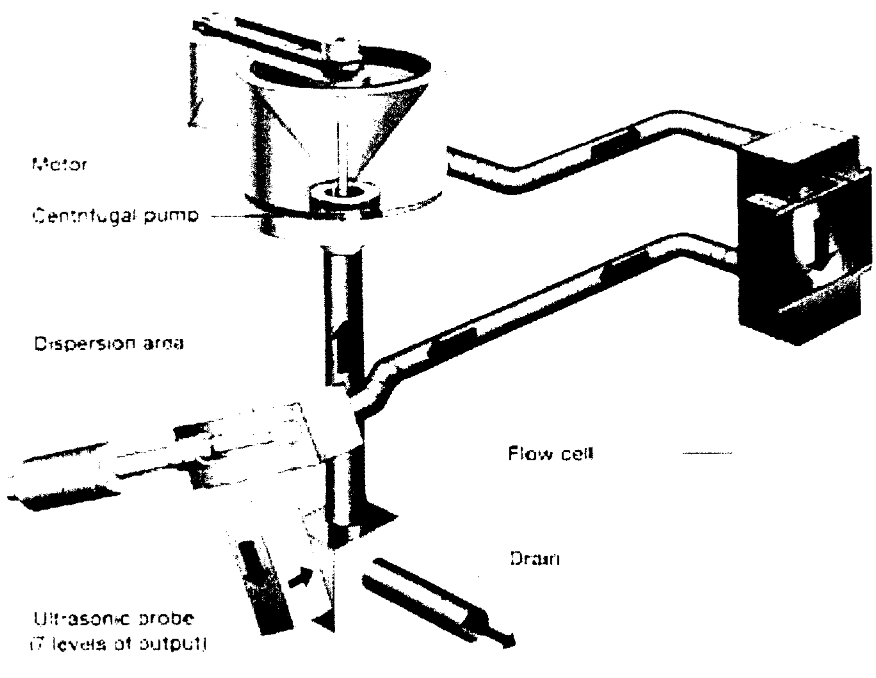

Figure 15: Horiba Sample Recirculation System

dispersed state due to surface charges), metal hydroxides, many chemical precipitates, and most organic substances other than true colloids.

If the "true" PSD is the non-sonicated case, the expected settling regime would be particulate settling due to the larger heavier particles and lack of cohesiveness. One would not expect the slow compression type settling that is observed. This again leads to the conclusion that flocculation could occur in the particle size analyzer and the sonicated PSD measures the smaller "fundamental" component particles in the sludge rather than floccules. Since these solids are believed to be formed by chemical precipitation in the tanks, the conclusion that the sludge is flocculent is supported by the quote given above at these particle sizes.

2.4 Sludge Density Measurements

The density of the solids are evaluated in an EDF written by Poloski [4]. The EDF reached the following conclusions:

- 75% interstitial liquid in sludge by volume
- 25% air-dried solids in sludge by volume
- 2.0 g/ml air-dried solids particle density

With the interstitial liquid SG (specific gravity) at approximately 1.2, the calculated tank farm sludge specific gravity would be 1.4.

Comparing these densities with other materials produces Figure 16. The solid materials shown in this graph are at the lower end of the density spectrum. Consequently, the sludge in the tank farm is relatively low-density. Since the oven-dried density of the solids was significantly higher than the air-dried density, the low density of the solids could be attributed to a large amount of hydrated water present in the crystalline structure of the particles.

Please note that these measurements involved air-drying the solids and then adding deionized water to reconstitute the sludge. Through this process, the interstitial liquid chemistry is significantly altered from the chemistry in the tank farm (e.g. pH, molar concentration of significant species, etc.). Changing the interstitial liquid chemistry can, in turn, change the solids surface chemistry. Changing the surface chemistry alters the so-called *zeta potential*, which is an indicator of how the solid particles interact with each other. Ultimately, the solids packing and interstitial liquid fraction can be significantly altered by the chemistry of the interstitial liquid (the particle density measurements should be unaffected). Even with this potential source of error, these RAL data are the best available tank farm sludge density data.

Changing the liquid phase composition can also alter settling type and rate. When the solids are washed (via washball) and transported to another tank, the ionic composition of the liquid should be significantly diluted. Further investigation on diluting the liquid phase and changes of settling type and rate of the solids should be a priority.

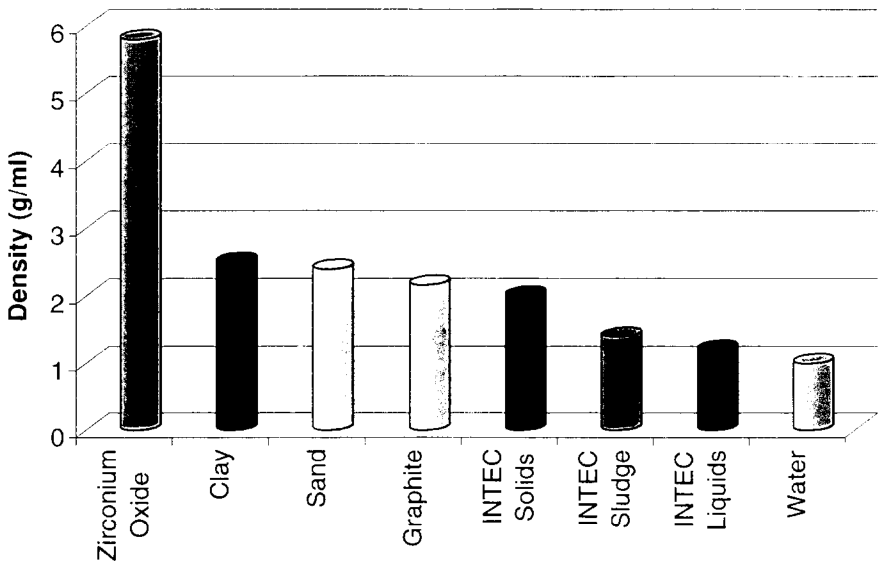

Figure 16: Density Comparison of Various Materials

2.5 Unknown Data and Risks

While the data discussed above provides a fairly comprehensive view of the many of the solids properties, we still do not have any empirical data on how the sludge will move when various degrees of force are applied. This empirical data would be very useful for the grout placement mockup because the grout applies a force to the sludge and displaces it. Being able to match these dynamic behaviors would allow for a much more accurate mockup.

Getting this empirical data would involve measuring the viscosity of the sludge under different conditions. Measuring the viscosity of the sludge would be achieved through the use of a viscometer. Currently, a viscometer is being prepared for deployment in the RAL hotcell for actual measurements of the sludge viscosity. Unfortunately, these data will be unavailable for this surrogate solids design effort. The high degree of variability between the viscosity of various materials under similar conditions is discussed below.

Most fluids are categorized as Newtonian. Newtonian fluids possess a linear relationship between shear stress (τ=force/area applied to fluid) and shear rate ($\frac{dv}{dy}$ = velocity profile of fluid). The slope of this linear relationship is referred to as the dynamic viscosity (μ) of the fluid. This relation is expressed in Figure 17.

When shear stress versus shear rate is measured and plotted a flow curve results. Flow curves are used to categorize fluids as one type of fluid or another. Fluids other than Newtonian are called non-Newtonian. Non-Newtonian fluids are fluids for which the relation between shear stress and shear rate is nonlinear or is linear but does not go through the origin (i.e. has a y-intercept other than zero). Often slurried material is categorized as a Non-Newtonian fluid. Flow curves for various types of fluids are shown in Figure 18.

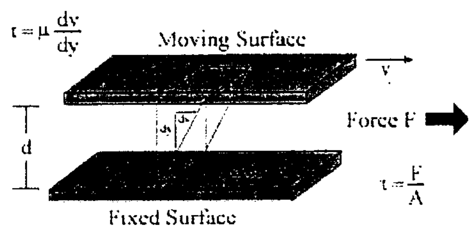

Figure 17: Definition of Viscosity

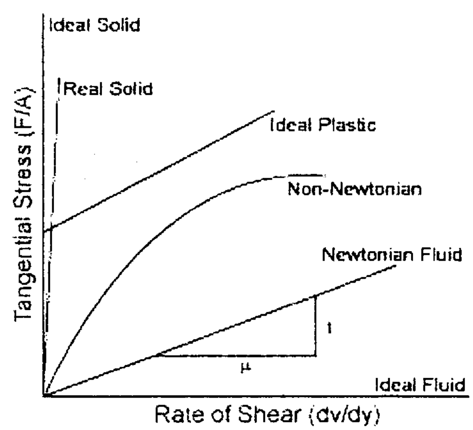

Figure 18: Flow Curves for Various Fluid Types

Examples of various materials and the type of fluid they are categorized are discussed below:

Newtonian (see Figure 19) Water, Most salt solutions in water, Light suspensions of dye, Kaolin (clay slurry), High-viscosity fuels, Gasoline, Kerosene, Most motor oils, Most mineral oils

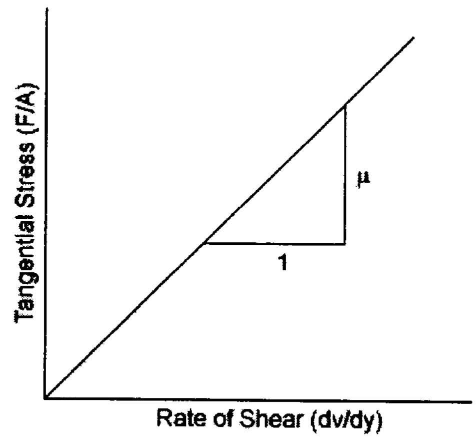

Figure 19: Newtonian Fluid Flow Curve

Yield Pseudoplastic/Bingham Plastic/Yield Dilatant (see Figure 20) Clay, Mud, Tar, Sewage sludge, Digested sewage, High concentrations of asbestine in oil, Thermoplastic polymer solutions

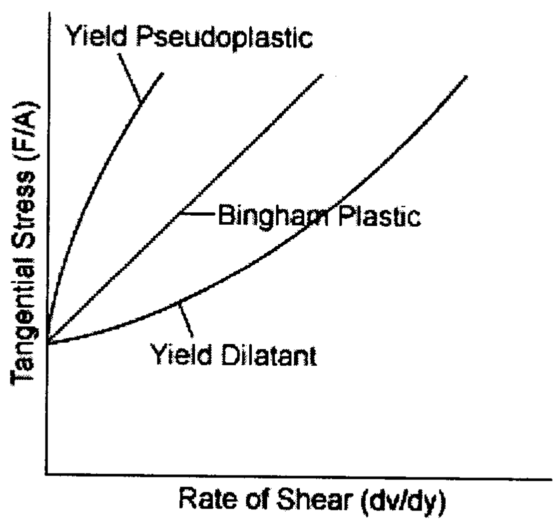

Figure 20: Flow Curves for Fluids with Yield Stresses

Pseudoplastic (see Figure 21) Sewage sludge, Paper pulp, Grease, Soap, Paint, Printer's ink, Starch, Latex solutions, Most emulsions

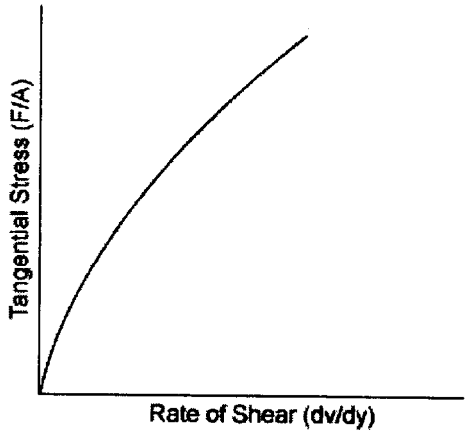

Figure 21: Pseudoplastic Flow Curve

Dilatant (see Figure 22) Feldspar, Mica, Clay, Beach sand, Quicksand, Starch in water

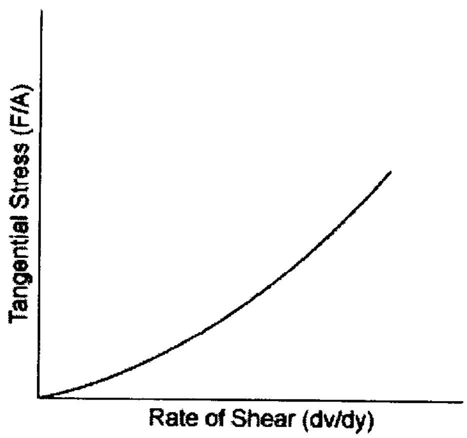

Figure 22: Dilatant Flow Curve

Thixotropic/Rheopectic (see Figure 23) Thixotropic – decreases viscosity over time/Rheopectic – increases viscosity over time, Inks, Most paints, Carboxymethyl cellulose, Silica gel, Greases, Asphalt, Starch, Bentonite, Gypsum solutions in water

As one can see, there is much variability in the behavior of these fluids. Since we do not have a flow curve for this the tank farm sludge there is an inherent risk that the surrogate sludge we use for mockups may not even be the same type of fluid. Consequently, we are

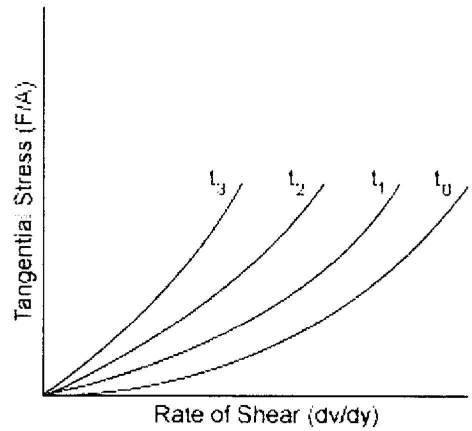

Figure 23: Time-Dependent Flow Curves

planning on creating a flow curve for our surrogate sludge prior to the mockup so when the tank farm sludge flow curve becomes available we can compare them. If the flow curves are significantly different, modifications to our surrogate sludge recipe could then be made.

2.6 Conclusions

In conclusion we are looking for a sludge with the properties listed in Table 1.

Significant Parameter	Tank Farm Solids
Low Yield Stress (from visual observations)	yes
Light, Billowy Sludge	yes
Flocculation Sedimentation	yes
Median Particle Size	8-12 micron
Particle Density	2.0 g/ml
Sludge Bulk Density	1.25 g/ml

Table 1: Significant Surrogate Selection Parameters for Tank Farm Sludge

3 Evaluated Surrogates

The surrogate sludge developed herein is based on limited measured physical and visual characteristics. It is desirous to develop a surrogate sludge that meets these characteristics, is inexpensive to produce, and minimizes industrial hygiene and environmental concerns.

Unfortunately, surrogate sludge development based on chemical characteristics could not be performed due to insufficient knowledge of chemical compound species within the TFF tanks.

Key technical parameters for determining the surrogate include the following (discussed above):

- remote video visual information during sampling operations within tanks WM-182 and WM-183
- solids settling rate of WM-183 sludge sample
- median particle size distribution
- particle (solids) and apparent (sludge) density

Based on limited analysis data from Tanks WM-182 and WM-183 samples, the liquid and solid (sludge) chemistry could not be estimated and an attempt to reconstruct a surrogate based on similar chemical species and viscosity could not be performed. The surrogate sludge was developed based on physical parameters - primarily video images displaying particle and rheological behavior, particle (solids) and apparent (sludge) density, solids settling rate, and median particle size distribution. Two Cole-Parmer rotational viscometers were purchased to determine shear rates as a function of shear stress. Unfortunately, the capability to use one these viscometers within the INTEC RAL Hot Cell has not been realized and there presently exists no viscosity (flow curve) data on TFF sludge. Viscosity measurements on surrogate sludge have not been made as there is no viscosity comparison criteria. It would be desirous to reasonably match the flow curve of the surrogate sludge to that of the actual sludge. This flow curve match would be particularly useful during grout displacement mock-up operations where one fluid (grout) flows into and interacts with another fluid (surrogate sludge).

It was envisioned that developing the surrogate sludge would entail adding a variety of materials to achieve these physical parameters as best as possible. A number of materials were examined during the investigation for surrogate development. Table 2 delineates the primary materials examined, marketing nomenclature, median particle size, density information, aimed surrogate uses, logistics issues, and particular health & safety issues. The types of materials for this investigation can be itemized into the following categories: minerals, clays, inorganic salts, polyelectrolytes, and bipolymers. The most important findings are addressed below.

3.1 Minerals

Several minerals were looked into as possible simulated sludge "building block" candidates due to their relatively low cost, chemically inert qualities, and environmentally friendly nature. However, success in finding a mineral meeting these criteria having a likeness to the actual sludge in median particle size, particle (solids) and apparent (sludge) density

Table 2: Evaluated Surrogate Materials

Material Category	Marketing Nomenclature	Median particle size (microns)	Specific gravity (particle density) and other densities	pH	Aimed surrogate uses	Logistics issues	Health & Safety issues (particular to the mock-up effort)
Mineral							
Talc	Pioneer 2606 lamellar 200 mesh talc from Zemex , sample from Suzorite Mineral Products P.O. Mineral products, Van Horn, TX 79855; (915)-283-2330	16.5	2.8 Loose bulk (lb/ft3) = 32; Packed bulk (lb/ft3) = 64	9.5	Bulk inert body for surrogate	Straight-forward and relatively easily logistics of adding feed and mixing the talc in water is anticipated. A very small percentage of the talc (just a surface film) appears to be strongly hydrophobic and stays on top of the water. It may be desired to decant this top portion off for easier viewing "into the water".	Possible airborne crystalline silica in excessive dusting
Iron oxide	Sample from Lansco colors - (201)-307-5995. May be able to buy locally.	**99.9% smaller than 44 microns [920 Black ave.=.5 micron, 415 Red ave.=.2 micron]**	5.18		Colorant for surrogate	Excellent colorant of suitable particle size. There exists reds, yellows, browns, and black colors of "iron oxide". Red is chosen as it has the highest chroma of all colors. It is desirous to color the surrogate sludge such that it can be visibly distinguished from grout during solids displacement and within core samples. A .2% by volume delivered a strong color to the surrogate.	None
Silicon Carbide (Black)	Electro Abrasives Corp. 701 Willet Road Buffalo, NY 14218 (716)-822-2500	**20 range = 5.5 - 31**	3.2		Bulk body or filler for surrogate	Extreme packing by settling in water because of blocky sharp particle shape (abrasive)	Nuisance dust, abrasive to tissue
Aluminum oxide (white fused)	Electro Abrasives Corp. 701 Willet Road Buffalo, NY 14218 (716)-822-2501	20	3.95		Bulk body or filler for surrogate	Extreme packing by settling in water because of blocky sharp particle shape (abrasive)	Nuisance dust, abrasive to tissue
Aluminum oxide (brown fused)	Electro Abrasives Corp. 701 Willet Road Buffalo, NY 14218 (716)-822-2501	20	3.95		Bulk body or filler for surrogate	Extreme packing by settling in water because of blocky sharp particle shape (abrasive)	Nuisance dust, abrasive to tissue
Zirconium alumina	Electro Abrasives Corp. 701 Willet Road Buffalo, NY 14218 (716)-822-2502	Very coarse particle size (too large)	4.3		Bulk body or filler for surrogate	No sample evaluation	Uncertain
Titanium dioxide (anatase and rutile)	None found	Could not find close particle size manufactured	3.89 & 4.25		Bulk body or filler for surrogate	Particle sizes tailored for pigment and ceramic industry and were too small	Nuisance dust

Table 2: Evaluated Surrogate Materials-Cont.

Material Category	Marketing Nomenclature	Median particle size (microns)	Specific gravity (particle density) and other densities	pH	Aimed surrogate uses	Logistics issues	Health & Safety issues (particular to the mock-up effort)
Graphite	World Sales Headquarters Asbury Carbons, Inc. PO Box 144, Asbury, NJ 08802, (908)-537-2155, www.asbury.com	**20**	**2.20-2.30**		Bulk body for surrogate	Extreme hydrophobic nature and surface tension making mixing impossible and messy without perhaps proper wetting with wetting agent	Fire risk from powder, respirable dust
Barium Sulfate	Barimite, CIMBAR Performance Minerals, PO Office Box 250, Cartersville, GA 30120, (800) 852-6868, www.cimbar.com	Mean particle size available as 1.8, 2.5, 4.0, 9.0, 11.0, 50.0	**4.5** Bulk dry loose and compacted densities vary widely with particle size- see company literature.	**7**	Bulk body or filler for surrogate. Can add as a percentage in the surrogate for conservatism due to very high particle density.	Inexpensive dense material and remote possibility of producing hazardous waste by generation of free Barium ions. Products represent group of naturally occurring unbleached products.	Possibility of producing hazardous waste by generation of free Barium ions?
Calcium Sulfate dihydrate (Hydrated Gypsum)	"Terra Alba #1", and "SNOW WHITE" United States Gypsum Company, 125 South Franklin Street, Chicago, Illinois 60606-4678, 1-800-621-9523	Terra Alba = 7, SNOW WHITE = **12**	**2.32** Loose bulk (lb/ft3) = 42; Packed bulk (lb/ft3) = 62	**7.3 for a 10% slurry**	Bulk body for surrogate. Weighting agent for clay/floc systems to speed settling rates.	Reasonable degree of packing in water - fair amount of stress to break solid when mixing, fairly quick settling time - with relatively clear supernate after 3 hours. Can be added to kaolin/iron oxide/alum mixture directly (before or after alum addition)	Possible airborne crystalline silica in excessive dusting
Calcium Carbonate	RO-40 & No. 8 White, LANSCO COLORS, 305 West Grand Ave., Montvale, NJ 07645, (201) 307-5855	25% retained on 74 micron wet screen and 44 mesh screen	**2.71**	**9.0-9.5**	Bulk body for surrogate	Fair degree of packing in water - fair amount of stress to break solid when mixing, fairly quick settling time - with relatively clear supernate after 3 hours.	None
Crystalline silica	Silica Quartzite, ARCO Hills, LLC., (208)-524-2657	200 mesh - all particles smaller than 74 microns	**2.464**	**5.9**	Bulk body or filler for surrogate	Uncertainties with particle size and the uncertainties associated with inhalation hazard of 100% crystalline silica.	Airborne crystalline silica in excessive dusting
Silica gel		Particle size uncertain - would have to be ground to match settling rate etc.	**2.1**	**3-8 in aqueous slurry**	Bulk body for surrogate	Particle size uncertain - would have to be ground to match settling rate etc.	Amorphous form so free of crystalline silica. However, the material has a moderate health rating. Inhalation causing dryness to mucous membranes, nose, and throat. Abrasion to eyes.

Table 2: Evaluated Surrogate Materials-Cont.

Material Category	Marketing Nomenclature	Median particle size (microns)	Specific gravity (particle density) and other densities	pH	Aimed surrogate uses	Logistics issues	Health & Safety issues (particular to the mock-up effort)
Diatomaceous silica	Diatomaceous Earth, DE (775) 352-1000	"Powder sized finer than 45 microns"	2 Dry density (lb/ft3) = 9.5-13.0	**7.0 -10.0 for a 10% slurry**	Bulk body for surrogate (A naturally occurring mineral derived form microscopic in size fossilized remains of marine diatoms).	Uncertainties with particle size and uncertainties associated with relative high crystalline silica. Very abrasive particle most likely not representative of sludge particle shape and dynamics.	Inhalation hazard. Uncertainties in the amount of crystalline silica.
Clay							
Wyoming Sodium Bentonite (Sodium Montmorillonite)	WYO-BEN, INC, P.O. Box 1979, Billings, Montana 59103	Varies, Standard 75-80% (% minus 74 microns), Fine grind (% minus 44 microns)	**2.45-2.55** Product bulk density around 55 lb/ft3	**8-10 (5% aqueous suspension)**	Seed for flocculent and body mass - Kaolin provides particles of anionic surface, which upon addition of flocculating agents such as Aluminum Sulfate, Ferric Sulfate, and Ferric Chloride destabilize and drop out of suspension much more quickly as larger particles.	Extreme control needed for mixing. Swelling clay in water (around 15X dry volume). Bentonite masses prone to gumming together. Gumming very much reduced with proper shearing, mixing, and hydration before bulk settling. Reasonably effective visual rheological characteristics. Floc size varies with variables not understood at this time.	Possible airborne crystalline silica in excessive dusting
Kaolin	WILKLAY FE, 325 Mesh Screen Residue, from Wilkinson kaolin Associates LTD., P.O. Box 306, Milledgeville Rd., Gordon, GA 31031; (912)-628-5301	**0.7**	**2.6**	**5.0 (28% solids)**	Seed for flocculent and body mass - Kaolin provides particles of anionic surface, which upon addition of flocculating agents such as Aluminum Sulfate, Ferric Sulfate, and Ferric Chloride destabilize and drop out of suspension much more quickly as larger particles.	Reasonable control needed for mixing. Non-swelling clay. Forms a typical clay film that may need a little physical pressure to clean completely off most surfaces.	Possible airborne crystalline silica in excessive dusting
Laponite (synthetic)	Southern Clay Products, Inc., 1212 Church Street, gonzales, TX 78629 (888)-Laponite or 830-672-2891		Bulk density = 0.7-1.3 kl/dm3 (packed)	**9.8** (2% dispersion in water)	Gel characteristics to provide yield stress and provide thixotropic rheolgy and suspending power for adding known particle sizes of other materials. Laponite is an entirely synthetic hectorite mineral which closely resembles the natural clay mineral hectorite (such as bentonite). Provides a clear gel unlike bentonite. Also possible seed for flocculent with addition of salts (particularly Laponite RD). Experiments in support of this assessment of adding aluminum sulfate into a laponite suspension produced a very lightweight sludge. Flocculated laponite produced opaque particles which settles very slowly.	Conventional mixer process control for mixing. Swelling clay but not prone to substantial gumming as bentonite. Very non-dense flocculent formed as a result of addition of alum. This floc may be difficult to separate in process.	Adding strong mineral acid may produce Lithium salts which may cause a RCRA concern (?). However, it does not contain free crystalline silica found as an impurity as in most other natural minerals.
Inorganic salt							
Aluminum Sulfate	Various	**NA**	1.69	**2.3+/-0.4 conc. aqueous solution**	Salt causing flocculation by diminishing zeta potential around clay particles	Relatively inexpensive salt that can be purchase either as liquid (usually 50 wt.%) or solid. Solution of Aluminum sulfate can have a pH as low as 1.9, but for use here should be well above the RCRA pH of 2.0 for any remaining liquid.	Harmful if swallowed or inhaled. Causes irritation to skin, eyes, and respiratory tract. Hazard minimized by purchasing in solution form. Precautions for splashing, eye potection, etc.

Table 2: Evaluated Surrogate Materials-Cont.

Material Category	Marketing Nomenclature	Median particle size (microns)	Specific gravity (particle density) and other densities	pH	Aimed surrogate uses	Logistics issues	Health & Safety issues (particular to the mock-up effort)
Ferric Sulfate	Various	NA	3.097 (Anhydrous)		Salt causing flocculation by diminishing zeta potential around clay particles	Known to form a gelatinous floc. Mixture of Ferric Sulfate and clays have not yet been prepared as part of this study due unavailability of Ferric Sulfate to date for this effort.	Harmful if swallowed or inhaled. Causes irritation to skin, eyes, and respiratory tract.
Ferrous Sulfate	Various	NA	1.9		Salt causing flocculation by diminishing zeta potential around clay particles	Known to form a gelatinous floc. Limited use of very low grade Ferrous Sulfate mixture. Mixture of Ferrous Sulfate and clays have not yet been prepared as part of this study due unavailability of Ferrous Sulfate to date for this effort.	Harmful if swallowed or inhaled. Causes irritation to skin, eyes, and respiratory tract.
Ferric Chloride	Various	NA	2.9		Salt causing flocculation by diminishing zeta potential around clay particles	Too corrosive for our use - formed a yellowish gel looking floc that may need to be examine if corrosive and health and safety issues are not an issue.	Very corrosive and an irritant. Not recommended for this effort due to health and corrosion hazard.
Magnesium Sulfate	Various	NA	1.67 (aqueous solution is neutral to slightly acidic)		Salt causing flocculation by diminishing zeta potential around clay particles	Produced a flocculent with kaolin clay but there was question whether the floc interparticle forces produces as positive rheological characteristics (visual yield stress, etc.) as with the trivalent aluminum sulfate.	None
Sodium Chloride	Various	NA	2.16	**6.7-7.3 (aqueous solution)**	Salt causing flocculation by diminishing zeta potential around clay particles	Produced a flocculent with kaolin clay but there was question whether the floc interparticle forces produces as positive rheological characteristics (visual yield stress, etc.) as with the trivalent aluminum sulfate.	None
Polyelectolyte							
many - Ciba Specialty Chemicals -(both cationic and anionic)	Ciba Specialty Chemicals Water Treatments, Inc. 2301 Wilroy Rd., Suffolk, VA 23439-0820 (757) 5380-3700	NA			Flocculation aid for dewatering, floc size, and increased floc settling. Available in non-ionic, anionic, and cationic. Product #455 (a low cationic ionic product) particularly produced very large fast settling floc with aluminum sulfate coagulated bentonite (also with iron oxide as colorant). Products #156 and #336 (anionic) were also tried with less successful results within the limited qualitative testing performed.	Must have proper preparation logistics established for making a concentrated polymer base stock. This consists of initially wetting the polymers with solvents of no or very little water such as ethanol, acetone, etc. This wetting process begins to "unravel" the long polymer chains without "gumming" the outer layers of the product particles causing inefficient dispersion in water because of the gum layer (poor water availability into the particle). This concentrate stock solution can then be diluted for uses as concentration needed. Must have adequately controlled mixing if to be used.	None - other than polymer wetting solvent management (relatively small amounts of ethanol, etc.)
Biopolymers							
Xanthan Gum	Kelzan AR Xanthan Gum, Kelco Biopolymers, 8355 Aero Drive, San Diego CA 92123 (800)-535-2687, www.kelco.com	NA		**7.2 1% solution**	Long chained polymers designed to directly change rheology characteristics of bulk mineral	Must have adequately controlled mixing if to be used. Biopolymer changed viscosity of hydrated gypsum in water to a lotion like consistency. Predicted same effect for talc, calcium carbonate, etc. Polyvalent cations may cause gelation at high pH.	Slipping hazard when wet

Table 2: Evaluated Surrogate Materials-Cont.

Material Category	Marketing Nomenclature	Median particle size (microns)	Specific gravity (particle density) and other densities	pH	Aimed surrogate uses	Logistics issues	Health & Safety issues (particular to the mock-up effort)
Welan Gum	K1A96 Welan Gum	NA			Long chained polymers designed to directly change rheology characteristics of bulk mineral	Must have adequately controlled mixing if to be used. Biopolymer changed viscosity of hydrated gypsum in water to a lotion like consistency. Predicted same effect for talc, calcium carbonate, etc. Polyvalent cations may cause gelation at high pH.	Slipping hazard when wet
Sodium carboxymethycellulose	AQUALON 7H4 sodium carboxymethylcellulose, Hercules Incorporated, Aqualon Division P.O. Box 271, Hopewell, VA 23860-0271, (801)-541-4679.	NA		6.5-8.5 1% solution	Polymer potentially used to directly change rheology characteristics of bulk mineral. An anionic water-soluble polymer derived from cellulose.	Must have adequately controlled mixing. Biopolymer changed viscosity of hydrated gypsum in water to a lotion like consistency. This product is considered hazardous according to the OSHA Hazard Communication Standard 29CFR1910.12000 due to the flammable dust potential.	Slipping hazard when wet. This product is considered hazardous according to the OSHA Hazard Communication Standard 29CFR1910.12000 due to the flammable dust potential.
Hydroxyethylcellulose	NATROSOL, Hydroxyethylcellulose, hercules Incorporated, Hercules Plaza, 1313 North market Street, Wilmington, DE 19894-0001	NA		6.0-8.5 1% solution	Polymer potentially used to directly change rheolgy characteristics of bulk mineral. A nonionic water soluble polymer derived from cellulose. Like AQUALON cellulose gum (sodium carboxymethylcellulose), it is a cellulose ether, but it differs in that it is nonionic and its solutions are unaffected by cations.	Must have adequately controlled mixing. Biopolymer changed viscosity of hydrated gypsum in water to a lotion like consistency. This product is considered hazardous according to the OSHA Hazard Communication Standard 29CFR1910.12000 due to the flammable dust potential.	Slipping hazard when wet. This product is considered hazardous according to the OSHA Hazard Communication Standard 29CFR1910.12000 due to the flammable dust potential.

was not adequate. The relatively low particle (solids) density of 2.0 g/ml and apparent (sludge) density of 1.25 g/ml (based on density data discussed above) presented density match challenges. In the beginning stages of this evaluation, the actual sludge settling rate was not known. Since free-falling settling velocity (see above particulate settling regime discussion) is a function of particle shape and density, it was desirous to match particle size (around 20 microns for samples), particle and wetted bulk minerals densities to develop the main body of surrogate of whose rheological properties could be modified. It was hoped that these mineral particles would provide the basis for mimicking particle suspension and settling needed for turbulent wash-ball mock-up activities.

Minerals such as calcium carbonate, silicon carbide, aluminum oxide, proved to have high interparticle wetted packing and thus very high slurry/sludge (water and mineral) density slurries, very fast particle/zone settling regime rates, and little observed rheological similarities to the TFF sludge. Of the minerals samples evaluated, talc and hydrated gypsum were the most promising. However, the sludge (mineral and water mixed) densities were determined to be as high as around 2.4 g/ml and 2.2 g/ml respectively. Compared to some of the other minerals examined, these sludge densities were quite low. Relative to flocculated clays (performed later in the investigation), the use of minerals such as talc and hydrated gypsum did not have the observed yield-stress rheological characteristics similar to the TFF sludge (see Figure 1). Because mineral sludge densities and settling rates (see Figure 24) were high for talc and hydrated gypsum compared to the actual sludge, clay flocculated systems proved a more promising mechanism for developing the surrogate. Please note that the type of settling observed for these mineral based surrogates was accumulation settling (see Section 2.2). The settling curves for these mineral based surrogates are then based on the uppermost interface between the suspension and supernatant liquid. Even with this conservative basis the mineral based surrogates settled at a much faster rate than the tank farm sludge.

Iron oxide, having a desirable particle size distribution, served as surrogate pigmentation of pre-flocculated clays and was not meant to be used as a bulk surrogate solid substrate. Iron oxide is an excellent colorant for the surrogate sludge. There exists red, yellow, brown, and black colors of iron oxide. Black results in a colored surrogate nearly identical to the actual sludge. Red would be a desired color for surrogate used during grout displacement mock-up activities as it as the highest chroma of all colors. It is desirous to color the surrogate sludge such that it can be visibly distinguished from grout during solids displacement and within core samples. It was found that about 0.2% by volume of surrogate was adequate color the surrogate. Less colorant could be sufficient.

3.2 Clays

Because the particle size distribution of clays are at least partially into the colloidal range, clays as a bulk surrogate ingredient are not be desired. Colloidal sized particles (0.001 μm to 1 μm) are stable in solution (remain suspended) and cloud (visible obscure) clarity of solution. Wyoming Sodium Bentonite (Sodium montmorillonite), kaolin, and laponite are

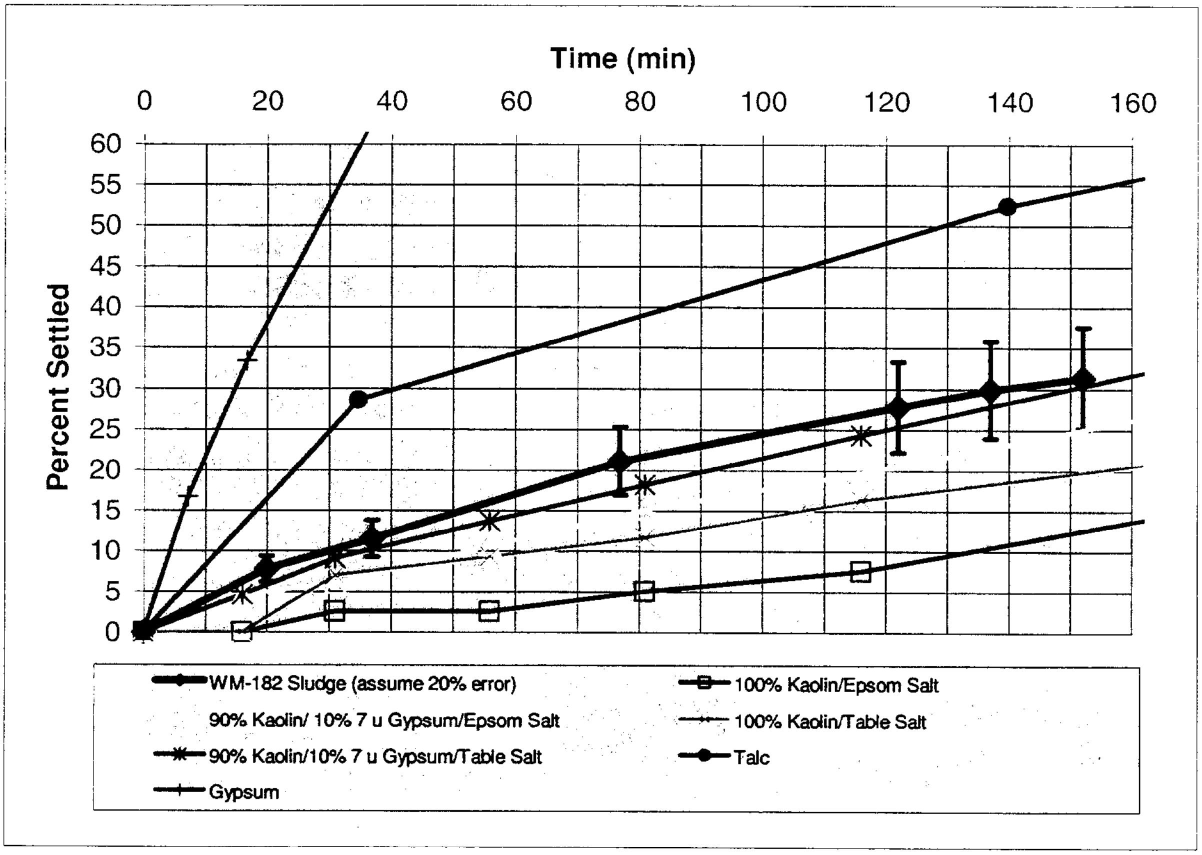

Figure 24: Evaluated Surrogate Settling Rates

clays that were examined for use as seeds for flocculation. In addition, laponite was also examined as a possible gelling agent for suspending particles. Bentonite and kaolin are opaque natural clays whereas laponite is a clear synthetic clay. Particles from these clays are anionic which upon the addition of flocculating agents become destabilized, increase in size out of the colloidal range, and settle out of solution. Bentonite and aluminum sulfate (alum) floc size appeared to vary greatly with salt-anion concentration and shear stress (mixing). The floc settled quite quickly resulting in a settled sludge that exhibited yield-stress rheological characteristics similar to the TFF sludge. Laponite, when flocculated with alum, produced an extremely non-dense (perhaps hard to manage) floc that would probably be of little use for the surrogate effort. This laponite base floc could perhaps be used as a percentage of another floc to decrease the overall sludge density. However, to use as a primary surrogate base the use laponite would not be acceptable. Kaolin clay flocculated with alum increased the median particle range from 0.7 μm (kaolin powder particles) to around 19 μm (kaolin/alum floc particles). These kaolin-based floc particles appeared to not agglomerate in lower shear rate conditions as did the bentonite and alum mixture. The settled flocculated kaolin clay was observed to exhibit yield-stress rheological characteristics very similar to the TFF sludge. Such similar observations between the actual sludge and kaolin/alum surrogate include:

- A "billowing" of particles from the top surface of the sludge upon slight disturbance
- Oscillation of the surrounding sludge from the point of disturbance similar to that of gelatinous material
- A relative rigidity of surrounding material directly near an area of sludge removal or relocation often leaving a "clumpy" appearance of the sludge
- A similar "cracking" appearance around an area of sludge removal or relocation.
- A similar settling appearance of zone/compression settling

These similarities will be discussed in greater detail in the next section.

3.3 Inorganic Salts

Trivalent, divalent and monovalent cations of salts were used to flocculate bentonite and kaolin. From the limited experiments performed to date, it appeared that the trivalent aluminum provided stronger yield stress characteristics than the did divalent magnesium (magnesium sulfate), and monovalent sodium (sodium chloride) with bentonite and kaolin. Therefore, the flocs created with epsom and table salts should not be considered for surrogate sludge. However, settling rate curves for these materials are shown in Figure 24.

3.4 Polyelectrolytes

It was desired to investigate the use of polyelectrolytes as flocculating aids to see if as a result of the flocculation process a desirable particle size and yield stress would be established. Many polyelectoytes samples were obtained from Ciba Specialty Chemicals (anionic, cationic, and non-ionic), three of which were tested with flocculated bentonite clay. Those chosen for this effort were Ciba MAGNAFLOC # 156 (anionic), # 336 (anionic), and # 455 (cationic). The use of these flocculent aids resulted in either no observed effect at the concentrations used or extremely large quickly settling rubber-like floc (up to 1.5 cm bridged floc) that did not show any interparticle behavior that would result in the observed TFF sludge yield stress characteristics. Upon further investigation and detailed lab work with the numerous polyelectroytes and also with the use of kaolin clay, it is possible that more promising results may be obtained. However, logistics issues probably make the use of polyelectrolytes unrealistic. Proper preparation logistics must be established for making a concentrated polymer base stock. This consists of initially wetting the polymers with solvents of no or very little water such as ethanol, acetone, etc. This wetting process begins to "unravel" the long polymer chains without "gumming" the outer layers of the product particles causing inefficient dispersion in water because of the gum layer (poor water availability into the particle). This concentrate stock solution can then be diluted for uses as concentration needed. Even though used small quantities relative to the mass to be flocculated, adequately controlled mixing must be established if polyelectolytes are to be used.

3.5 Biopolymers

Biopolymers are long chained polymers investigated to directly change rheological characteristics of bulk material commonly used in the food, pharmaceutical, and personal care formulations. Xanthan gum, Welan gum, Sodium carboxymethylcellulose (CMC) and Hydroxyethylcellulose are biopolymers that were mixed with the bulk inert mineral gypsum to investigate a likeness to the observed rheological behavior of the TTF sludge. In all cases the biopolymers changes the viscosity of hydrated gypsum in water to a lotion like consistency. These biopolymers, mixed with talc, calcium carbonate and other bulk minerals for this effort are anticipated to have the same effect. The mixtures did not exhibit the clumping, cracking yield stress characteristics of the observed TFF sludge. Also, the biopolymers require adequately controlled premixing preparation, the logistics of which make then an unlikely choice for the TFF mock-up. The bioploymers must be mixed very well before entry into the media in which they are to affect the rheology. In general, the use of biopolymer rheology modifiers with minerals did prove to be as effective because the mineral particles are entrained/restrained within the polymer substrate and the mixture of bulk material and the mixture tends to have a elastic viscosity characteristics such as lotion or syrup. The rheological characteristics thought to be caused by the attractive interparticle forces as displayed by flocculated clay systems could not be mimicked by the mineral biopolymer combination.

3.6 Conclusion

After evaluating the materials previously describe above, it was determined that kaolin clay (pigmented with iron-oxide) flocculated by the addition of aluminum sulfate (alum) provides the basis for an effective surrogate. A detailed comparison of kaolin/alum floc to tank farm sludge is given in the following section.

4 Recommended Surrogate

4.1 Visual Data

Visually, the kaolin/alum sludge exhibits the characteristics discussed in Section 2.1. First, we placed a tube in the kaolin/alum sludge layer (see Figure 25). Suction was then applied to the tube to mimic the LDUA sampling events. From this procedure, the following characteristics were realized:

- a cylindrical depression was created when the sludge is removed through the suction tube
- surface cracks formed around this depression
- some of the sludge was agitated and billowed into the liquid phase

Next, the sample tube was moved through the sludge layer (see Figure 26) in an attempt to mimic the similar WM-182 event discussed in Section 2.1. This motion created a wake behind the tube. From this wake, one can see a similar type of yield stress property where large sludge clumps were formed around the wake boundary.

Finally, a kaolin/alum sludge was placed in a bottle similar to the WM-182 sludge RAL sample bottle. Note that black iron oxide pigment was used. As the bottle was tipped to one side, a similar property to the WM-182 RAL sludge was observed, the sludge layer did not shift with gravity (see Figure 27).

In conclusion, the kaolin/alum sludge visually exhibits the low yield stress properties exhibited in the tank farm sludge.

4.2 Settling Type and Rate

The kaolin/alum based sludge was agitated and allowed to settle. A slow zone/compression regime was observed. Volumetric measurements were made and Equation 1 was used to compute the percent settled parameter. The results are shown in Figure 28. Note that six runs were performed and the kaolin/alum sludge settled consistently slower than the WM-182 observed rate. Since slower settling would result in a larger quantity of solids being transferred from the washball tank during the mockup, a faster settling sludge is required.

Because of its low density, hydrated gypsum at 7 μm and 12 μm was selected to be added to the kaolin/alum floc. Roughly measuring by volume, a 90% kaolin 10% hydrated

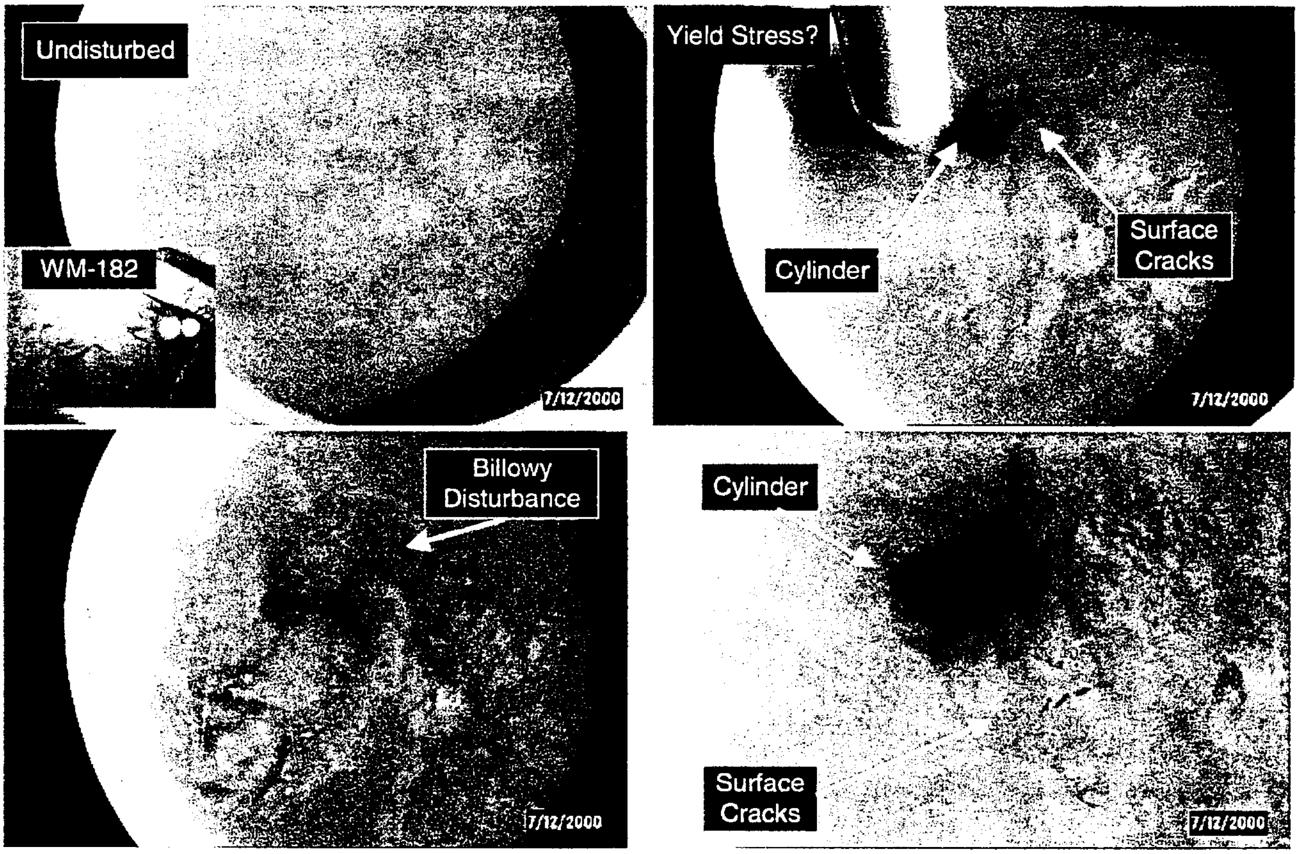

Figure 25: Sampling the Kaolin/Alum Sludge with a Suction Tube

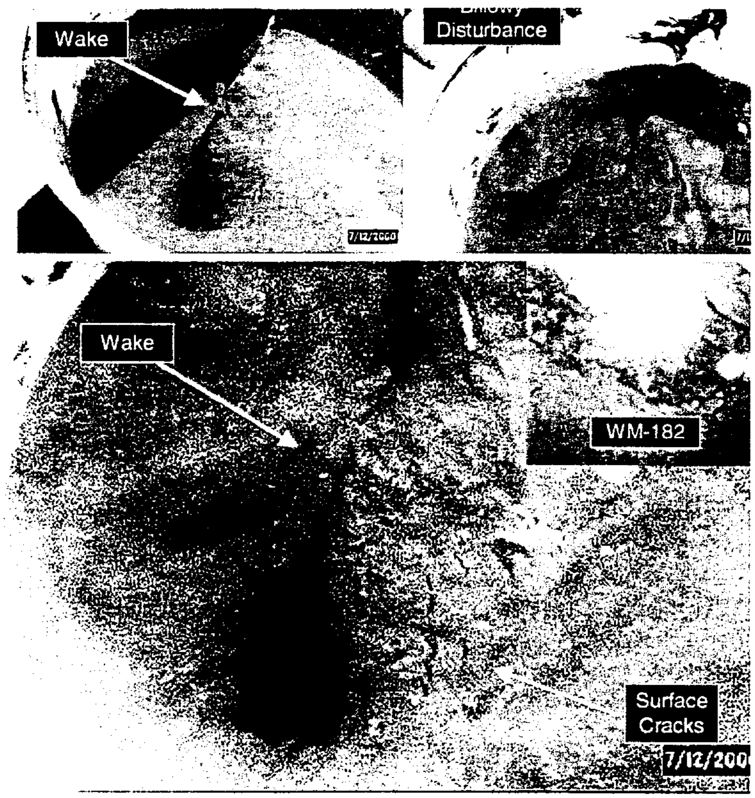

Figure 26: Moving the Suction Tube through the Kaolin/Alum Sludge

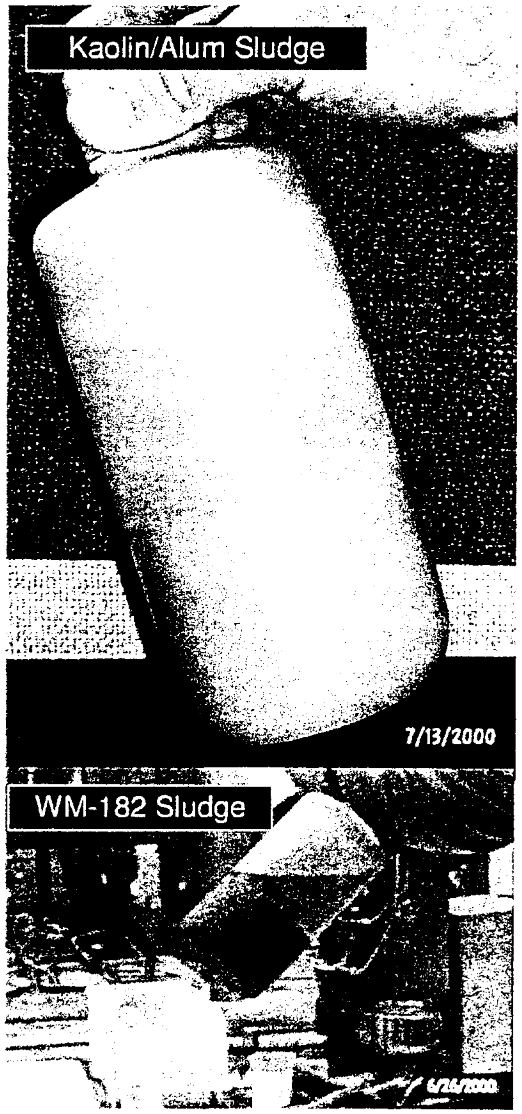

Figure 27: Tilting the Kaolin/Alum Sludge

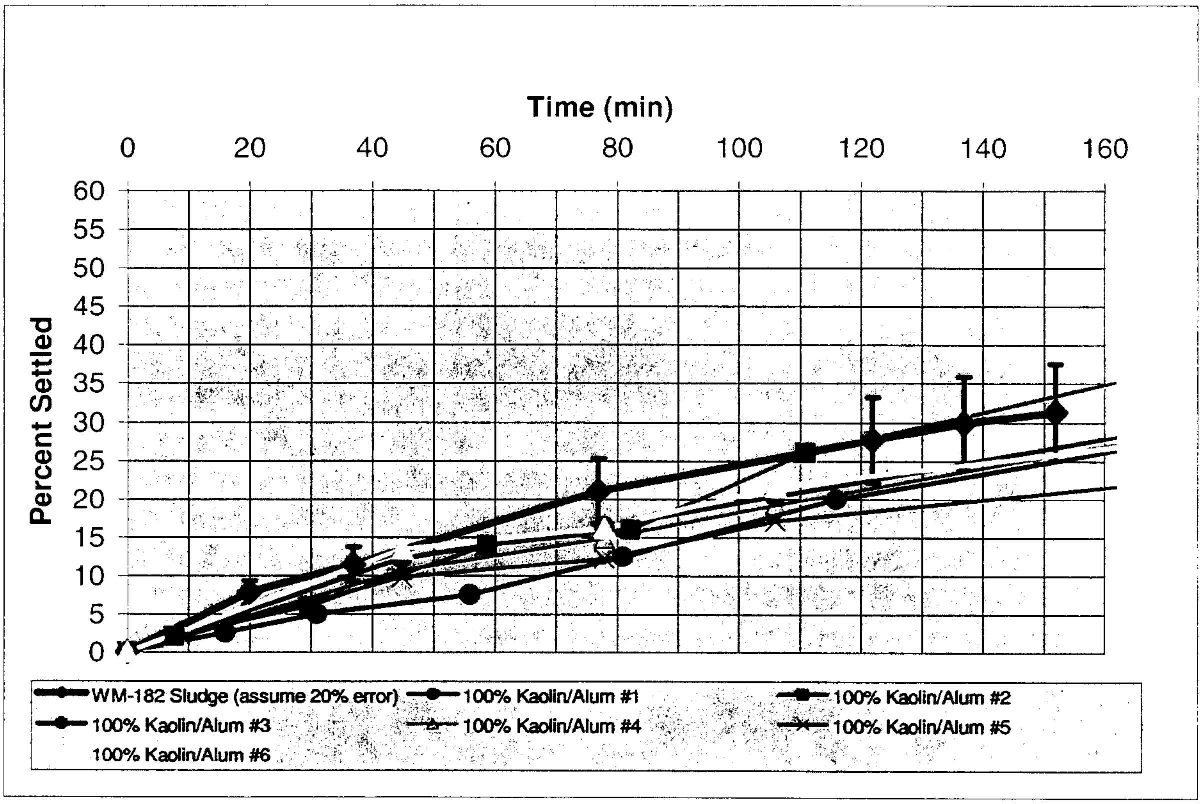

Figure 28: Kaolin/Alum Compression Settling Rate

gypsum slurry was prepared at both particle sizes. The sludge was agitated and allowed to settle. Volumetric measurements were made and Equation 1 was used to compute the percent settled parameter. The results are shown in Figure 29. These results show that the addition of a relatively small amount of gypsum acts as a settling agent and significantly reduces settling time. The addition of the hydrated gypsum also does not adversely effect the visual comparisons made above. However, bulk volumetric measurements of powders is yields poor repeatability due to variations in powder packing. Therefore, the exact amount of gypsum added to the surrogate recipe will be determined in the future on a mass basis when analytical balances become available.

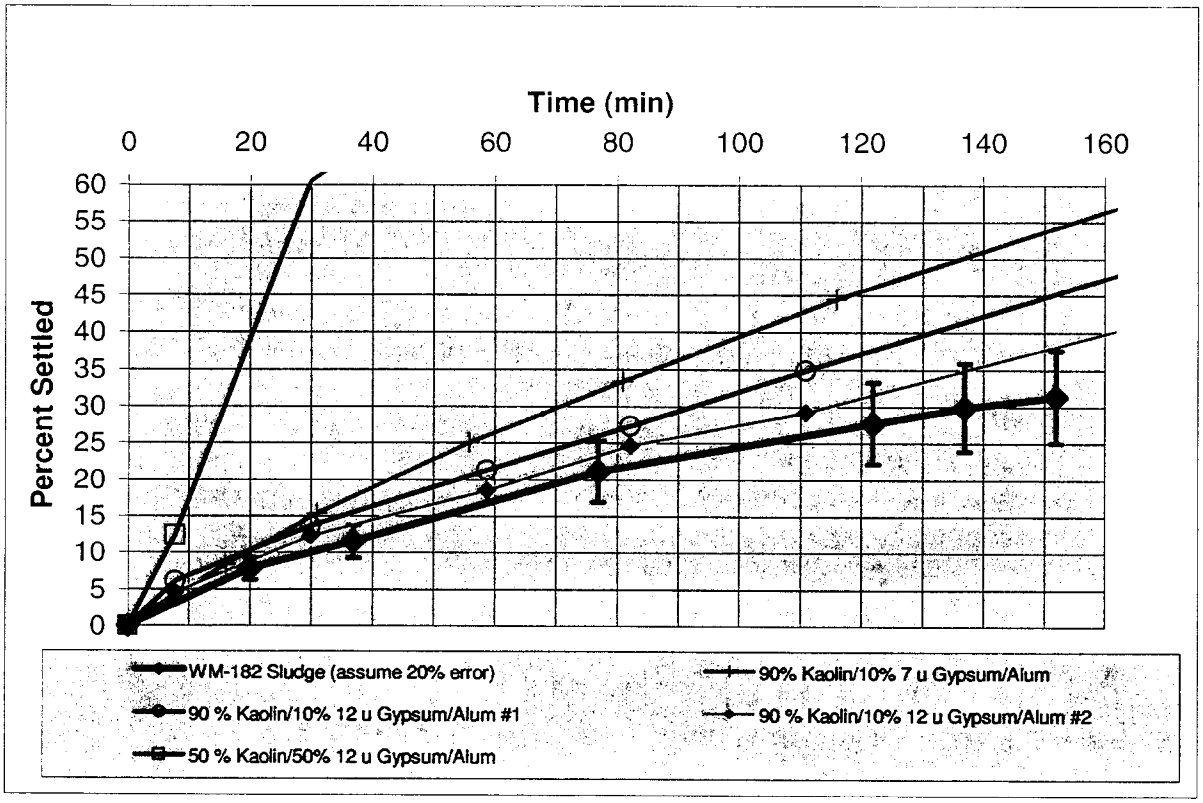

Figure 29: Kaolin/Alum/Gypsum Compression Settling Rate

Note that Iron Oxide was used in these sludges as a pigment. Adding Iron Oxide after the flocculating agent resulting in the pigment becoming one large mass and difficult to disperse. Therefore, the Iron Oxide pigment must be added before the flocculating agent (alum).

4.3 Particle Size Distribution

Since the particle size analyzer we used to make measurements on our candidate sludges consists of a mechanical agitator to keep the sludge dispersed (i.e. a Coulter counter), we should compare fundamental particle size to fundamental particle size and our target PSD should be based on the sonicated data set. For WM-182, the median sonicated particle size is approximately 8 μm. The WM-183 median sonicated particle size is approximately 12 μm. The average particle size distribution for the kaolin/alum/iron oxide sludge (based on four runs) is shown with the sonicated WM-182 and WM-183 PSDs in Figure 30.

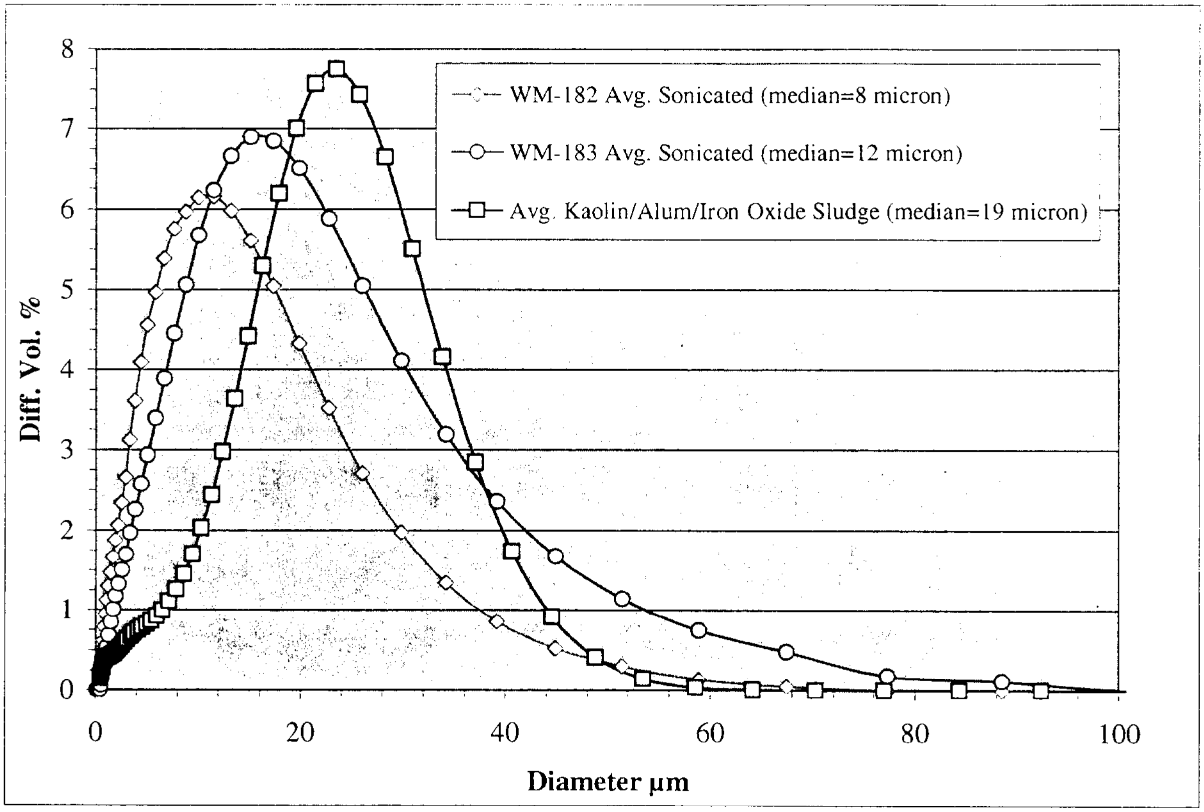

Figure 30: Kaolin/Alum/Iron Oxide Particle Size Distribution

In conclusion, the median particle size for the kaolin/alum/iron oxide sludge is relatively close to the WM-182 and WM-183 particle size medians.

4.4 Sludge Density Measurements

The particle density of kaolin is given in vendor data as 2.6 $\frac{g}{ml}$. Sludges typically have a interstitial liquid fraction in the range of 70% to 90% by volume. This range is consistent with rudimentary experiments with the kaolin/alum sludge of 75% to 86% interstitial liquid by volume. Using the more liberal 70% to 90% interstitial liquid range the expected sludge density should be in the range of 1.16 $\frac{g}{ml}$ to 1.48 $\frac{g}{ml}$. This range encompasses the tank farm sludge density of 1.25 $\frac{g}{ml}$. A comparison of the expected kaolin/alum density values and the tank farm sludge density values are shown in Table 3.

Description	Tank Farm Sludge Parameter	Expected Surrogate Parameter	Units
Percent Interstial Liquid	75	70-90	%
Percent Solid Particles	25	10-30	%
Solids Particle Density	2.0	2.6	g/mL
Interstial Liquid Density	1.0	1.0	g/mL
Bulk Sludge Density	1.25	1.16-1.48	g/mL

Table 3: Expected Kaolin/Alum Densities

5 Conclusions

It was determined that kaolin clay (pigmented with iron-oxide) flocculated by the addition of aluminum sulfate (alum) provides the basis for an effective surrogate. Calcium sulfate dihyrdate (hydrated gypsum) provides effective adjustment of settling rate and particle size. Quantitative work needs to be performed in order to develop final recipe ratios of the surrogate solid ingredients. Because of the wide variation in dry apparent (bulk) densities (and therefore volumes) of many minerals/clays such as kaolin clay, it is desired to perform future recipe development based on mass measurements. To date, measurements have consisted of volume measurements and estimations. A comparison of the tank farm sludge and the kaolin/alum sludge is summarized in Table 4

Significant Parameter	Tank Farm Solids	Kaolin/Alum Sludge
Low Yield Stress (from visual observations)	yes	yes
Light, Billowy Sludge	yes	yes
Flocculation Sedimentation	yes	yes
Median Particle Size	8-12 micron	19 micron
Particle Density	2.0 g/ml	2.6 g/ml
Sludge Bulk Density	1.25 g/ml	1.16-1.48 g/ml

Table 4: Significant Surrogate Sludge Selection Parameters Comparison

Below is a summary list of the chosen surrogate benefits:

- The combined surrogate constituents can be percentaged to compare very closely to the settling rate and particle size distribution of the WM-183 actual sludge.
- No acidic or basic solution required as part of the process make-up (other than the coagulating agent Aluminum Sulfate which has mild acidic properties).
- Materials are inexpensive.

- Materials are safe to use.

- Generation of the surrogate sludge and disposal of the surrogate sludge will not be regulated as hazardous waste under the Resource Conservation & Recovery Act (RCRA).

- All materials can be mixed together in two steps. The kaolin, iron oxide, and gypsum are to be mixed in the first step to homogenize the mixture, followed by the alum addition. The mixing process is easy and can most likely be done with efficiency in a cement truck mixer. There are no special premixing requirements for preparing stock solutions.

- The particles in the material exhibit a particle size distribution similar to that of Tanks WM-182 and particularly WM-183 - the bounding tank for the simulated solids mock-up effort sludge depth and species denotation.

- The material exhibits a yield stress (based on visual observations) that matches the visual of the LDUA video footage of WM-182 and WM-183 sampling operations. The flocculated clays have provided more of the inter-particle forces needed for this behavior. The use of biopolymer rheology modifiers with minerals have not proven as effective as the mineral particles are entrained/restrained within the polymer substrate and the mixture of bulk material and the mixture tends to have a elastic viscosity characteristics such as lotion or syrup. More investigation may show different results.

- The mixed and then settled material results in two distinct phases, the sludge and the clear supernate.

- The mixture exhibits two settling characteristics as follows:

  - Upon complete disturbance of the sludge, the particles of such increased density (close proximity to one another) that a settling zone develops as the particles move in a defined horizontal layer enmasse as a moving filter capturing all particles via gravity settling. In this settling one may three distinct areas within a settling vessel - a clear supernate, a settling zone of particles, and the settled zone.
  - Upon partial disturbance of the sludge, the particles "billow" up from the sludge surface and then randomly settle until the supernate is clear. There is no distinct horizontal zone settling in this case.

- Material is easily colored with iron oxide of similar particle size. The color stays with the surrogate sludge (solids). The supernate remains clear. Red iron oxide is chosen over black, browns, and yellows for it has the highest chroma value and can be visually seen the easiest.

In addition, some of the issues associated with actually using this surrogate are discussed below:

- The beneficial properties of the sludge seem to deteriorate over time. After aging two to three weeks, the solids seemed to settle significantly faster and the yield stress properties seemed to degrade. Therefore, if the mockups are performed immediately following sludge production this degradation should be minimized.

- After approximately three weeks the kaolin/alum sludge had some algae growth. Therefore, a fungicide may be added to prevent biological activity.

- Please note that when washing occurs in the tank farm tanks, the interstitial liquid chemistry is significantly altered from dilution (e.g. pH, molar concentration of significant species, etc.). Changing the interstitial liquid chemistry can, in turn, change the solids surface chemistry. Changing the surface chemistry alters the so-called *zeta potential*, which is an indicator of how the solid particles interact with each other. Ultimately, the solids packing and interstitial liquid fraction can be significantly altered by the chemistry of the interstitial liquid. In addition, this dilution process can significantly alter the rheology of the sludge. Currently, the magnitude of these changes is unknown. Therefore, we have tried to match the sludge to the current tank farm conditions and no effort has been made to mimic this potential dynamic system.

References

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A Flocculation Theory

Since the fundamental concept behind surrogate development involves flocculation, the following provides a brief introduction to some basic concepts of colloids, coagulation, and flocculation [1].

Many minerals, some organic pollutants, proteinaceous materials, some algae, and some bacteria are suspended in water as very small particles. Such particles, which have characteristics of both species in solution and larger particles in suspension, range in diameter from about 0.001 μm to about 1 μm. These particles are classified as colloids. Colloids may be classified as hydrophilic colloids, hydrophobic colloids, or association colloids. Hydrophobic colloids interact to a lesser extent with water and are stable because of their positive or negative electrical charges. The charged surface of the colloidal particle and the counterions that surround it compose an electrical double layer (adsorbed-ion layer and counter-ion layer), which causes the particles to repel each other. Colloidal particles are thus prevented from aggregating. Hydrophobic colloids are usually caused to settle from suspension by the addition small quantities of salts that contribute ions to solution. Clay particles are examples of hydrophobic colloids.

Destabilization of charged particles in water occurs as a result of the type of chemical (usually inorganic salts) causing coagulation. These salt ions reduce the electrostatic repulsion between particles to such a extent that the particles aggregate. Because of the double layer of electrical charge surrounding a charged particle, this aggregation mechanism is sometimes called double-layer compression. The selection of type and dosage of the chemical coagulant must be made by experimentation, most commonly with "jar tests." For this effort, 150 ml graduated beakers were primarily used to measure the volume of floc produced. Coagulation involves the reduction of this electrostatic repulsion, such that colloidal particles of identical materials may aggregate. Flocculation depends upon the presence of bridging compounds, which form chemically bonded links between colloidal particles and enmesh the particles in relatively large masses called floc networks.

Polyelectrolytes of both natural and synthetic origin may cause colloids to flocculate. Polyelectrolytes are polymers with a high formula weight, normally contain ionizable functional groups, are long enough for one end to adsorb onto one particle and the other end onto a second particle (bridging). Somewhat paradoxically, anionic polyelectolytes may flocculate negatively charged colloidal particles. The mechanism by which this occurs involves bridging between the colloidal particles by way of the polyelectrolytes anions. Strong chemical bonding has to be involved, since both the particles and the polyelectrolytes are negatively charged. The flocculation process induced by anionic polyelectrolytes is greatly facilitated by the presence of a low concentration of a metal ion capable of binding with the functional groups on the polyelectolyte. The positively charged metal ion serves to form a bridge between the negatively charged anionic polyelectrolytes and negatively charged functional groups on the colloidal particle surface. Acrylamide, polyacrylamides, polystyrene sulfonate, polyacrlyate, polyvinyl pyridium, and polyethylene amine are examples of synthetic polymers.

For a synthetic polyelectrolyte to function effectively, it must be released from its transported state to be available as a free dissolved and fully extended single molecule. Sophisticated modern polymers are supplied in solid form for reasons of economy and ease of transportation and storage with the solid having a particle size distribution around a centrally selected mean. Each particle is a hard packed tangle of long polymer chains similar to a ball of string. For the individual chains to be released they must firstly absorb water to begin to uncoil by hydrating and activating their repulsive ionic groups. Unfortunately, the wetted polymer on the outer surface of each particle forms initially into a highly viscous gel which resists the passage of the free water necessary for wetting the polymer in the center of the particle. Thus, this initial absorption of water is dependent on the particle size.